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THE

PHYSICAL REVIEW.

A PHOTOGRAPHIC STUDY OF SOUND PULSES BETWEEN CURVED WALLS AND SOUND AMPLIFICATION BY HORNS.

By Arthur L. Foley.

Synopsis.

Photographic Study of Sound Pulses Passing between Walls Corresponding to Sections along a Straight Tube, a Crooked Tube, a Megaphone and a Conical Horn Receiver.—Using the photographic method previously developed by the author, four pairs of brass plates, each of the proper section, were arranged radially about the axis of the sound-producing spark so as to provide the four passages to be studied. As the sound pulse progressed through these passages, instantaneous photographs registered its position at various stages. Six of these are reproduced. They clearly show that whenever a pulse moves at an angle to a wall there is reflection in exact accord with Huygen's construction. Sound pulses, therefore, do not glide around bends in tubes without appreciable reflection. In the case of a pulse emerging from the open end of a tube or horn, the per cent. of the energy reflected is small, while much of the energy of a pulse entering the large end of a conical horn is reflected back out of the end it entered.

Sound amplification produced by four horn receivers of different flares and with ratios of end areas varying from 7.8 to 256 was roughly measured outdoors and also in a special room with sound-absorbing walls, using both a Rayleigh disk and a Webster phonometer. The amplifying factors found were from three to twenty times less than would be expected from the simple condenser theory, which is clearly untenable. It is concluded that the amplification is a result of both resonance and condensation.

Prevailing Theories.

That the sound energy falling upon the ear or other form of sound receiver may be considerably increased by placing the receiver at the small end of a conical horn is a matter of common observation. The correct explanation of the amplifying action of the horn is quite another matter. In the opinion of the writer the complete explanation has not yet been given. Certain it is that the horn is not merely a condenser, nor is it merely a resonator. The former idea is the most common and the farthest from the truth. Doubtless many of us have

thought of a conical horn as a sound condenser through which sound passes like liquid or shot through a funnel. Most textbooks that say anything at all about horns give substantially such an "explanation."

Quoting from one of the older books: "The reinforcing action of the ear trumpet has been attributed to the successive reflections of the sound waves, which multiplies their action on reaching the tympanum. But, as in the speaking trumpet, experiment has shown that the influence of the walls, and consequently the reflection of their inner surface, is very feeble, if any at all. The effect produced is in reality owing to the progressive diminution of the sections of the air surface which transmit the sound and which then transmit it with increasing energy towards the organ. This effect may be compared with that of a jet of water which issues from the orifice of a hose with much greater force than a body of water of equal diameter in the interior of the pump barrel."[1]

Quoting from one of the latest textbooks: "The ordinary speaking tubes connecting distant rooms in buildings depend not on regular reflection, but on the fact that the air particles next the inner surface of the tube vibrate most easily parallel with the surface; this causes the direction of vibration to be deflected by gradual bends in the tube, and consequently the wave runs along the tube without reflection. In ear trumpets, by the constraint of the smooth walls of the tube, the wave entering the wide end is gradually diminished in area till it emerges at the small end carrying all the energy that entered at the large end. Thus if the large end is 100 times that of the small end, *the energy per cubic centimeter* in the emergent wave is 100 times as great as in the wave which entered the trumpet, neglecting loss by friction, etc."[2] The redeeming word in this explanation is "etc."

Over against the notion that the horn is a condenser we have the statement that it is a resonator. "The effect of the horn is to reinforce the the vibrations which enter it due to the resonance properties of the air inclosed by the horn. . . . The horn is an air resonator . . . the response below the fundamental of the horn is very feeble."[3]

Quoting from the classic treatise of Lord Rayleigh:[4] "The case of progressive waves moving in a tube of variable section is also interesting. In its general form the problem would be one of great difficulty; but where the change of section is very gradual, so that no considerable alteration occurs within a great many wave lengths, the principle of energy will guide us to an approximate solution. It is not difficult to see that

[1] Guillemin, Application of Physical Forces, p. 114.
[2] A. L. Kimball, College Physics, Revised Edition, pp. 196–197.
[3] Dayton C. Miller, The Science of Musical Sounds, pp. 156 and 159.
[4] Lord Rayleigh, The Theory of Sound, Vol. II., p. 63.

in the case supposed there will be no sensible reflection of the wave at any part of its course, and that the energy of the motion must remain unchanged . . . from which it follows that as the waves advance the amplitude of vibration varies inversely as the square root of the section of the tube. In all other respects the type of vibration remains absolutely unchanged. From these results we may get a general idea of the action of an ear trumpet. It appears that according to the ordinary approximate equations there is no limit to the concentration of sound producible in a tube of gradually diminishing section."

In the light of the theory of reciprocity[1] it is difficult to harmonize the above statement with one by the same author a few pages later when speaking of the action of a trumpet. "From the theory of diffraction it appears that the sound will not fall off to any great extent in a lateral direction, unless the diameter of the large end exceed half a wave length. The ordinary explanation of the effect of a common ear trumpet, depending on a supposed concentration of the *rays* in an axial direction, is thus untenable."[2]

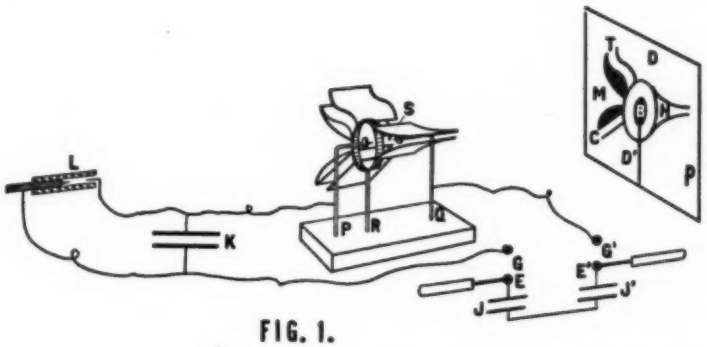

FIG. 1.

In view of such conflicting opinions, the writer decided to subject the question to experiment; by photographing sound waves passing through channels and by measuring the increase in intensity of a sound at a point when a conical horn is used as a "condenser."

Photographic Method.

Figure 1 is intended to show only the general principles of the photographic method used. Details of the light gap, "camera" box, spark control, etc., may be found in some of the writer's earlier papers.[3]

[1] Ibid., Vol. I., p. 150.

[2] Ibid., Vol. II., p. 102.

[3] A New Method of Photographing Sound Waves, Phys. Rev., XXXV., Nov., 1912, p. 373.

J and J' are capacities, each of from one to five Leyden jars, averaging 525 cm. each, connected to the electrodes E and E' of an electric induction machine capable of producing sparks twenty to thirty centimeters long. The spark gaps G, G', S and L are in series. When the capacity J, J' is discharged through the gaps G, G', sparks pass at both S and L. The spark at S takes place between platinum terminals at the ends of the brass rods P and Q and produces a sound wave. By properly adjusting the length of the light spark L (1 to 3 cm.) and the capacity K (six to twenty Leyden jars), the light spark can be retarded until the sound wave produced by the sound spark at S has had time to travel a short distance radially outward from the axis of the sound spark. Then when the light spark occurs, it casts a shadow of the sound wave on the photographic dry plate P.[1] B is the shadow of hard rubber buttons placed on the rods at each end of the sound spark gap to minimize the fogging of the dry plate by the light from the sound spark.

In order to study the passage of sound waves between walls and plates, several plates were cut from sheet brass, and shaped and disposed about the sound spark as shown in the figure. The plates were supported by soldering them at one corner to a narrow brass ring, the ring being placed beyond the end of the spark gap so as to interfere but little with the wave produced by the sound spark. The rod R, supporting the ring, and the rods P and Q were placed in line with the light gap so that they cast but one shadow on the dry plate.

The writer was not very successful in photographing sound waves through transparent tubes and horns. The curvature of the walls of the tubes so interfered with the passage of the light through them that the waves could be photographed only at points along the axes of the tubes. The writer concluded, therefore, to curve some plates and so place them with respect to one another and to the sound spark axis that a vertical section at right angles to the spark axis would correspond to a longitudinal section of a tube or a horn. The shadow of plates so disposed, shown in Fig. 1, is the projection of such a section. Thus C represents a longitudinal section of a straight cylindrical tube, T a crooked tube, M a megaphone, and H a flared conical horn. For convenience they will be designated, respectively, straight tube, crooked tube, megaphone and horn. The spaces between the megaphone and the tubes on each side were closed to bring out more clearly their outlines. In the directions D and D' the wave was free to travel without interference from reflecting surfaces.

Except in so far as sound intensity affects sound velocity, it would appear that the shadow of a cylindrical sound pulse passing between plates

[1] Proc. Ind. Acad. Sci., 1915, p. 305.

curved and disposed as shown in the figure should represent a longitudinal section of a spherical pulse through tubes to whose longitudinal section the plate shadows correspond. Further, that the wave form in cylindrical tubes and horns for spherical pulses of the same radii as the cylindrical pulses would be obtained in the case of all but the crooked tube by rotating each system about its longitudinal axis.

It might be urged that we are dealing here with a sound pulse and not a sound wave. The writer[2] has shown that the velocity of such a pulse, except for points very near the spark axis, is the same as the velocity of a train of sound waves. Indeed, the pulse is more than a condensation only. In a study not yet published the writer has found that an electric spark produces both a condensation and a rarefaction and that the disturbed air shell near a spark is one wave length thick. But more to the point is the fact that the wave pictures show that the waves are exactly where we should expect them to be by Huygen's construction.

Figures 2 to 7, inclusive, show successive stages of an expanding spark wave, the average time interval between each of the six wave positions being about 0.00003 sec. Figure 3 is a double exposure, with a time interval of only 0.000006 sec. As would be expected, all six pictures show that the waves passed through the straight tube and megaphone without appreciable reflection, and that the megaphone wave suffered the greater attenuation. But on examining the waves through the crooked tube and through the horn we find convincing evidence that what has occurred is not just what some of us have been thinking would happen in such cases.

All the pictures show that there was energy reflection in every case except when the wave front was at right angles to the surface and the motion of the air parallel to the surface of the tube. In the case of the horn there was continuous reflection from one end to the other, even at the small end where the angle of the cone is very small. In the case of the crooked tube there were successive reflections. For the crooked tube, Fig. 6 and Fig. 7 show respectively an emerging and emerged wave much more attenuated than in the case of the straight tube of the same size. A considerable portion of the wave energy appears to be trapped inside the tube. However, it will be observed that the reflected waves in general were headed toward the outer end of the tube. This is not true, however, of the horn. Here the advancing wave shows unmistakable evidence of intensity increase or condensation, and that it emerged from the small end of the horn considerably amplified. But most of the energy was lost so far as the small end of the horn is concerned. The

[2] Proc. Ind. Acad. Sci., 1915, p. 299; 1918, p. 221. PHYS. REV., N.S., XVI., Nov., 1920, p. 449.

lost energy was contained in the reflected waves which, as the photographs show, headed the wrong way—"backing out" of the horn.

INTENSITY MEASUREMENTS.

Some sound intensity measurements substantiated what the photographs clearly suggest, that the condensing power of a horn is not the quotient of the areas of the two ends, that it is not even of the same order of magnitude in the case of horns of considerable angle.

The source of sound was an organ pipe blown by air from a tank in which a constant pressure was maintained by an electrically driven compressor. Intensity measurements were made with both the Rayleigh Disk[1] and the Webster Phonometer.[2] The intensity was measured at a given point, without horn. Then the horn was placed in position and the intensity measured again — at the same point. The quotient of the latter intensity by the former is called the amplifying power or amplification. If called the condensing power it should be remembered that it includes the amplification due to resonance.

The chief difficulty encountered in these measurements was due to reflection from the walls of the room. In a room 25×35 feet, except for certain well-defined interference regions, the sound was about equally intense everywhere and was practically the same when the receiving horn faced the source as when turned in the opposite direction. Then, too, the intensity was practically independent of the direction of the axis of the sounding organ pipe with respect to the receiving horn, and it varied but little with change of distance between source and receiver.

The apparatus was then set up out doors as far as possible from buildings, trees, and objects that would act as reflectors. The two chief sources of trouble outside were ground reflection and varying air currents. However, fairly consistent intensity measurements were obtained.

The most reliable results were obtained when the apparatus was set up in a double-walled, constant temperaure room in the basement of the physics laboratory. The room was practically sound proof for sounds originating outside. To reduce the reverberation the walls were covered with the material which could be had quickest and without expense. Amongst other things there were several hundred large gunny sacks and a number of lap robes, blankets and comforters. The absorption was by no means all that could be desired. But it enabled the making of measurements in substantial agreement amongst themselves and with those made out doors, and sufficiently reliable to disprove the statement that a horn is a condenser.

[1] Rayleigh, Theory of Sound, Sec. 253b.

[2] Webster, Proc. Nat. Acad. of Sc., Vol. 5, May, 1919, p. 163. Ibid., July, 1919, p. 275.

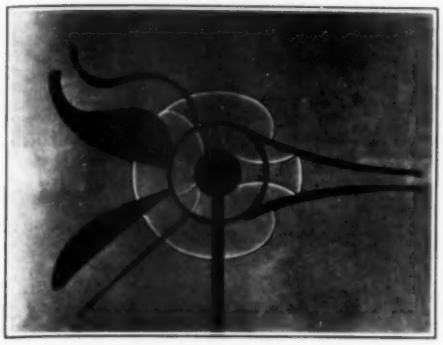

Fig. 2.

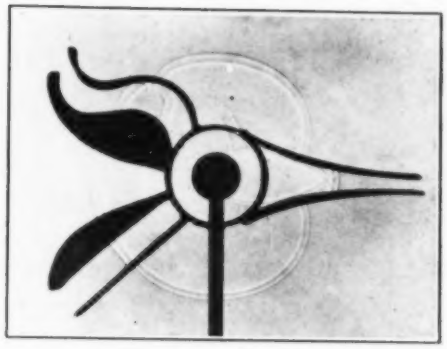

Fig. 3.

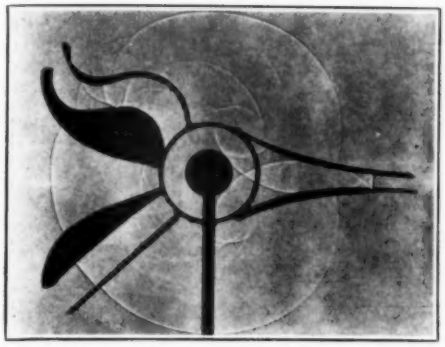

Fig. 4.

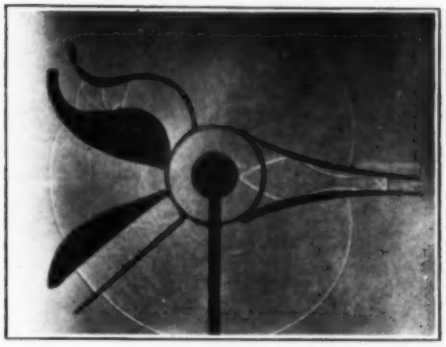

Fig. 5.

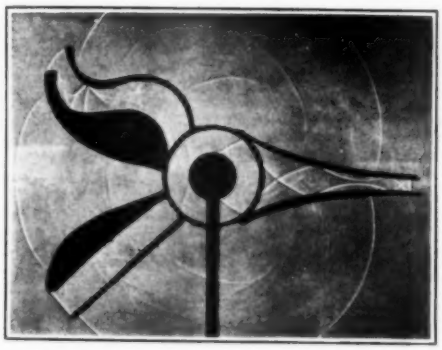

Fig. 6.

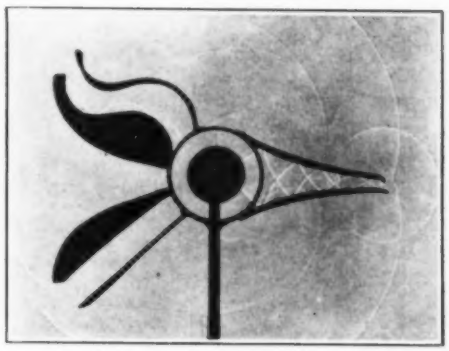

Fig. 7.

A. L. FOLEY.

Measurements were made with organ pipes of different pitch placed at different distances from the receiving apparatus. The horns used, four in number, were made of sheet zinc. All were thirty inches long when measured along the axis, and one and one quarter inches in diameter at the small end. The large end diameters were such that the ratios of the areas of the large and small ends were respectively 7.8, 33, 122, and 256.

Inasmuch as this experiment is to be repeated under wider and more favorable conditions than previously obtained, the writer will defer any extended publication and discussion of data. The following table, however, indicates the general character of the results:

Distance between Source and Receiver.	Ratio of End Areas of Horns.	Amplifying Factor.	
		By Rayleigh Disk.	By Webster Phonometer.
8.0 feet	7.8	3.1	2.9
8.0 "	33.0	7.9	4.3
8.0 "	122.0	11.9	6.0
8.0 "	256.0	13.0	7.3
6.5 "	7.8	2.6	2.0
6.5 "	33.0	9.1	4.3
6.5 "	122.0	10.3	6.0
6.5 "	256.0	8.3	6.5

The author attaches no importance to the data in the above table from the standpoint of their absolute values. There is no question, however, as to the order of the quantities involved. This being true, the condensing power of horns is not even approximately what it has been represented to be by many writers. For instance, if the "condenser" theory were true, the amplifying power of the larger horn should be 256 (neglecting friction — small in this case). The average of the four values given in the table is 8.8. The highest amplification obtained was 13, about one twentieth the theoretical value.

It will be noted that the intensity ratios given by the Rayleigh disk run higher than those given by the Webster phonometer. This may be due to the fact that the Rayleigh disk was suspended in free air — without resonator or enclosure — while the vibrating disk of the phonometer was mounted at the end of a cylindrical resonator. At such limited distances between source and receiver and with a sound as intense as that produced by an organ pipe (frequency 256), the phonometer was so sensitive it could not be used when its resonator was in tune with the source. Therefore, the phonometer was not used as designed to be used, with both disk and resonator in unison with the sound to be measured. The disk only was so adjusted.

The resonance theory of horn amplification requires that some of the energy of an emerging wave be reflected back into the horn. Figures 2 to 7 show that in the case of a spark wave the amount of the energy reflected at the open end of a pipe or horn is too small to give any trace of a reflected wave.

CONCLUSIONS.

1. The amplification of sound at the small end of a conical receiving horn is due to *both* resonance and condensation.

2. The amount of sound energy "condensed" at the small end of a conical horn receiver is but a small fraction of that demanded by the "condenser" theory. This theory is not tenable.

3. Sound pulses do *not* "glide around bends" in tubes and "slip" along slanting walls "without appreciable reflection." There is reflection at a surface whenever the molecules of air next the surface vibrate in any direction not parallel to that surface. Huygen's construction applies in every case.

4. Much of the energy of the waves reflected in a crooked tube of small angle may eventually emerge at the far end, but the several waves arrive at different times. Thus the form of the emerging wave may be widely different from that of the entering wave.

5. Much of the energy of a wave entering the large end of a conical horn is reflected and eventually *leaves the horn at the end it entered*. The wider the horn angle the greater the per cent. of energy thus "lost."

6. Of the energy of an emerging sound wave the per cent. reflected at the open end of a tube is small.

WATERMAN INSTITUTE FOR RESEARCH.
INDIANA UNIVERSITY.

AN EXPERIMENTAL INVESTIGATION OF THE DISPERSION OF A LIMITED WAVE TRAIN.

BY IRVIN H. SOLT.

SYNOPSIS.

Dispersion by a Prism of a Limited Train of Hertzian Waves, 7.8 and 9 cm. Long.—According to the theory developed by Sommerfeld, Brillouin, and Colby, some energy should be propagated through the prism undeviated, the proportion decreasing as the angle of incidence is increased. This conclusion has now been experimentally confirmed. To insure a large number of short wave trains, a pliotron circuit adjusted to a frequency of 170,000 cycles was used to energize a modified Righi vibrator consisting of two steel balls suitably mounted close together. The waves so generated were sent as a parallel beam through an opening in a wall to a 30° pitch prism, and the energy as a function of the angle of deviation was determined by means of a molybdenite crystal detector, in series with a sensitive galvanometer, placed at the focus of a parabolic mirror. Various possible sources of error were eliminated or corrected for. The undeviated energy was found to decrease from 26 per cent. for 0° incidence to 8 per cent. for 35° incidence, in general agreement with the theory.

Index of refraction of pitch for Hertzian waves, 7.8 cm. long, was found to be 1.99.

INTRODUCTION.

IN the neighborhood of an absorption band the index of refraction of a dispersing medium may be less than unity and consequently the velocity with which a given wave crest in a monochromatic wave train is propagated may exceed its velocity in vacuum. This is true only after the medium has reached a steady state, *i.e.*, theoretically, for an infinite wave train. From this one might conclude that a signal could be sent with a velocity greater than the velocity of light in vacuum in contradiction to the principle of relativity. A signal, however, must differ from an infinite monochromatic wave train in that it has some peculiarity of form, a beginning or an end, by means of which it can be identified. Sommerfeld [1] was the first to attack this problem theoretically, taking as his signal the limited sine wave

$$f(t) = \sin \frac{2\pi t}{P}, \qquad \text{for } 0 < t < T,$$

$$f(t) = 0, \qquad \text{for } t < 0 \text{ and } t > T,$$

incident perpendicularly on the dispersing medium. He expresses the signal in the form of a Fourier integral which represents the sum of an infinite number of infinite wave trains. Having done this he applies

[1] Sommerfeld, Ann. d. Phys., 44, p. 177, 1914.

the ordinary dispersion theory and obtains an integral representing the disturbance, a distance x in the dispersing medium, as a function $f(t, x)$ of t and x, which he evaluates by Cauchy's method of integration in the complex plane. The result shows that in all cases, including the region of anomalous dispersion, the front of the wave train arrives at a point x in the medium in a time $t = x/c$ and consequently travels with vacuum velocity. The amount of energy which arrives at a given point with this velocity is very small and consists of waves which are very short compared with the incident radiation.

The work of Sommerfeld was extended by Brillouin,[1] who treated the complex integration of the integral $f(t, x)$ more exhaustively. He defines the arrival of the signal as the moment when the amplitude of the disturbance reaches half its final value. Colby[2] investigated the case of oblique incidence, both with reference to form and direction of propagation of the first part of the disturbance. He showed that in this case also the wave front is propagated with vacuum velocity and is undeviated at the boundary. As time goes on the disturbance in the medium swings continuously toward the normal until the steady state is reached when it has the direction required by the ordinary law of refraction. The period of the first part of the disturbance is very short and the amplitude very small. Both quantities decrease with increasing obliquity, and increase as time goes on, the latter passing through a maximum and minimum before the steady state is reached.

Consider now a wave train incident on a prism (Fig. 1). According to the theory outlined above, the front of the wave train will pass through the prism undeviated and arrive at the point A on the arc ABC. The succeeding part of the disturbance will arrive at consecutive points the emerging beam after the steady along AB, OB being the direction of state has set in. The disturbance which arrives at points between A and B is a transient effect which precedes the establishment of the steady state. It is the object of this investigation to detect this effect experimentally.

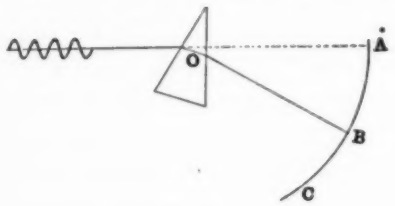

Fig. 1.

Since the effect we are investigating is very small and associated only with the beginning of a wave train, it is essential to use a source of radiation which emits a very large number of short wave trains per

[1] Brillouin, Ann. d. Phys., 44, p. 203, 1914.
[2] Colby, PHYS. REV., V., 3, 1915.

second. The limited sine wave assumed by Sommerfeld cannot be realized experimentally. The most convenient type of radiation to use is the highly damped wave emitted by a Righi vibrator. In this case most of the energy will be in the first period and hence the effect we are looking for will be a larger proportion of the total energy than would be the case if a longer wave train were used.

THE VIBRATOR.

The source of radiation was a slightly modified form of Righi vibrator similar to the type frequently used in recent work [1] with short Hertzian waves. It consisted of two steel balls .95 cm. in diameter resting in sockets ground in a glass holder, or held between strips of wood. For an air gap and electric vector horizontal the holder shown partly in Fig. 2*A* was used. It was made as follows: A piece of glass tubing 35 cm. long and .95 cm. in diameter was bent in the shape of a wide *U*, having vertical sides 8 cm. long. The horizontal portion was then bent into a loop until the vertical sides almost touched. A glass tube sealed to the under side of the loop serves as a support. It is fastened to a horizontal slider which makes it possible to adjust the balls accurately at the focus of the parabolic reflector. The gap between the balls was adjusted by means of a thin piece of glass forced between the two nearly parallel vertical portions of the holder.

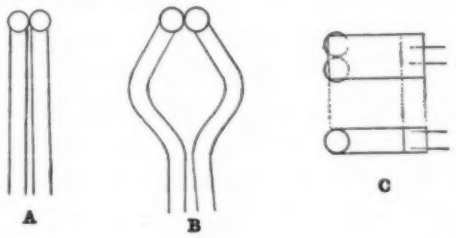

Fig. 2.
Different methods for holding vibrator.

When an oil gap was used the holder was similar to the above except that the vertical parts were bent out immediately below the balls, as shown in Fig. 2*B*. This permitted the oil to flow away freely and reduced to a minimum fouling of the gap due to deposits of carbon from the decomposing oil. To keep the balls firmly seated it was necessary to connect the holder to a filter pump. Paraffine lubricating oil was contained in a reservoir above the reflector whence it flowed through a glass tube and issued from a capillary nozzle a few millimeters above the gap. The spent oil was caught in a receptacle immediately below the reflector, and was used repeatedly, being filtered occasionally to remove the carbon.

[1] Webb and Woodman, PHYS. REV., XXIX., p. 89, 1909; Woodman and Webb, PHYS. REV., XXX., p. 561, 1910; Severinghaus and Nelms, PHYS. REV., I., p. 411, 1913; and others.

Some observations were made with the electric vector vertical. In this case the two balls were held between two thin strips of wood, 1.7 cm. by 2.8 cm., one end of which was glued to a piece .9 cm. square and 1.7 cm. long (Fig. 2*C*). A glass rod waxed to the latter served as a support.

The leads to the vibrator consisted of brass wire 2 mm. in diameter passing through ebonite bushings in the reflector immediately behind the vibrator. The ends were rounded off and a short piece bent over 45°.

The reflector was a sheet of silver-plated copper in the form of a paraboloid of revolution, having an aperture 50.8 cm. in diameter, a depth of 13.8 cm. and a focal length of 11.4 cm. It was mounted on a rigid stand with its axis horizontal and 155 cm. above the floor.

As pointed out above, it is necessary that the vibrator emit a large number of wave trains per second. To satisfy this condition the alternating potential used to excite the vibrator must have as high a frequency as possible. At first a 10-in. induction coil operating on 60 volts and a mercury jet interrupter giving about 900 interruptions per second were employed. The oil gap already described was used with this coil. It was necessary to regulate the current through the gap by means of a large water resistance in series with the secondary of the induction coil. When this was not done the gap readily fouled and the vibrator became very erratic.

The observations taken with the induction coil will be discussed later. They indicated the existence of the effect, but the galvanometer deflections for small deviations were only a few millimeters. It was therefore desirable to replace the induction coil by some device which would give a higher frequency. This was accomplished by means of the pliotron circuit shown in Fig. 3. The essential features of this circuit are a large inductance and a small capacity.[1] The inductances L_1, L_2 were about 5 millihenries each wound in four

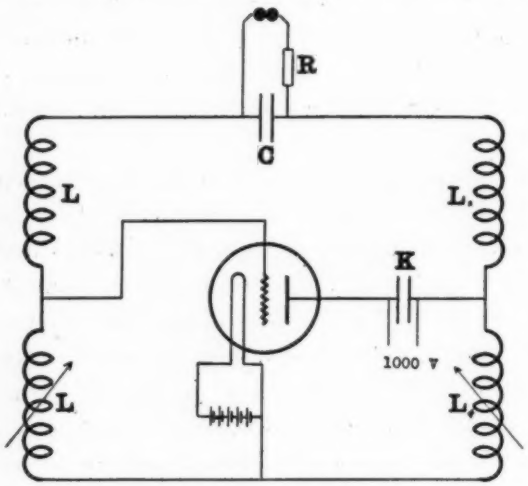

Fig. 3.
Pliotron circuit.

[1] W. C. White, Gen. Elec. Rev., Aug., 1917.

units. Each unit consisted of from 60 to 75 turns of No. 20 wire diameter and 20 cm. long. L_3 and L_4 were of wound on a wooden polygonal frame, the winding being 30 cm. in the variometer type, the settings being usually about .1 and .5 millihenry respectively. The condenser C consisted of two sheets of tin 45 cm. by 50 cm. supported on four glass rods passing through holes near each corner, and separated by pieces of glass tubing 10 cm. long fitting over the glass rods. The water resistance R was necessary to prevent the oscillatory discharge of the condenser C, through the circuit containing the vibrator. Two type P pliotrons were used in parallel. At the frequency employed (170,000) the energy emitted by a vibrator with an oil gap is no greater than with an air gap; since the sparks pass so rapidly that a bubble of vapor is always in the gap. Consequently the air gap described above was used exclusively. In this connection it is interesting to note that Bartenstein[1] and Lindmann[2] used a Tesla transformer to excite a vibrator partially or totally immersed in oil. It is doubtful whether the presence of the oil in this case increased the energy emitted by the vibrator except in so far as it increased the wave-length.

The adjustment of the circuit was somewhat critical. The tendency of the spark gap was to emit a musical note, indicating that the oscillations in the pliotron circuit died down after each spark and required a large number of cycles to be built up sufficiently for another spark to pass. With proper adjustment the spark made a noise resembling that due to a blast of air from a fine nozzle.

The Receiver.

The type of receiver most commonly used for quantitive work with electric waves has been that devised by Klemenčič.[3] It consists of two narrow copper wings joined together by a thermocouple which is connected to a sensitive galvanometer. For maximum sensitivity the galvanometer must be of the low resistance, moving magnet type which is frequently tedious to work with. Sjöström[4] has recently described a crystal detector which he claims is more sensitive than the thermocouple type, besides having the advantage of high resistance. The receiver used in the present work was a modified form of the type developed by Sjöström. A cross section of it is shown in Fig. 4.

Two brass rods b, b', 10 cm. long and .5 cm. in diameter, screw into brass cylinders c, c', which are held in an ebonite cylinder a. The hole

[1] Bartenstein, Ann. d. Phys., 29, p. 201, 1909.
[2] Lindmann, Ann. d. Phys., 38, p. 523, 1912.
[3] Klemenčič, Wied. Ann., 42, p. 416, 1891.
[4] Sjöström, Diss. Upsala, 1917.

in the cylinder c ends in a shoulder against which a thin flake of molybdenite d is pressed by the rod b. The rod b' ends in a blunt point which makes contact with the flake. A glass tube e, 40 cm. long, serves as a holder. The galvanometer leads are soldered to c, c', closely twisted and passed through the glass tube. The main receiver was placed at the focus of a parabolic reflector having the same dimensions as that used with the vibrator and mounted on a stand the same height above the floor.

The resistance of such a receiver is high, of the order of several thousand ohms. This fact makes it possible to obtain high sensitivity using a d'Arsonval galvanometer. Two high sensitivity moving coil galvanom-

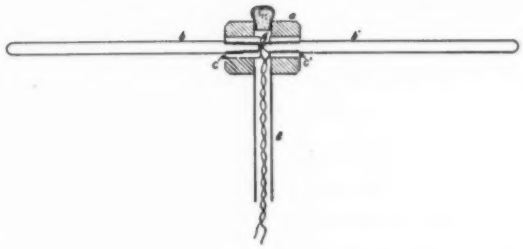

Fig. 4.

The receiver.

eters made by the Leeds and Northrup Company were used. The one connected to the main receiver had a sensitivity of 2.5×10^{-10} ampere and a period of 8.5 seconds, while that connected to the check receiver had a sensitivity of 5×10^{-10} ampere and a period of 6 seconds.

THE PRISM.

The dispersing medium was a pitch prism with a refracting angle of 30°. The faces were 75 cm. high and 85 cm. long. It was cast in a wooden box which was retained throughout the work. The sides of the box were made separately of 1-in. yellow pine boards, being held together by two bolts at each vertical edge.

ARRANGEMENT OF THE APPARATUS AND METHOD OF OBSERVATION.

The final arrangement of the apparatus is shown in Fig. 5. The oscillating system S and the check receiver C were in one room, while the prism P, the main receiver M and the galvanometers G were in an adjacent room. The radiation passed through an aperture 50 cm. in diameter in the center of a metallic screen A about 270 cm. square covering the doorway and adjacent part of the wall. In the doorway, between this screen and the prism was a cylindrical screen B, 50 cm. in

diameter and 100 cm. long. The object of the screening is to let no radiation enter the room in which the main receiver is located except that which passes through the prism.

The prism was mounted on a turntable which permitted a rotation of 40°, the axis of rotation intersecting the axis of the parabolic mirror at *S*. The mounting was adjusted so the angle of incidence could be varied from 0° to 40°, and the prism was placed as close to the screen *B* as the maximum angle of incidence permitted.

The distribution of energy in the spectrum produced by the prism was measured by moving the main receiver along the arc of a circle *D* having a radius of 200 cm., the axis of the receiving mirror always inter-

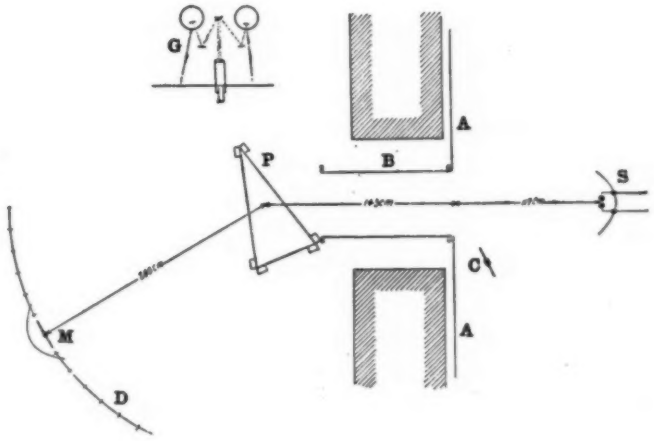

Fig. 5.

secting the axis of rotation of the prism. To take account of the variation of the energy emitted by the vibrator a check receiver *C* was employed. It was located about 100 cm. from the vibrator and just out of the beam of radiation passing through the aperture in the screen *A*.

The two galvanometers were located side by side on a wall bracket (*G*, Fig. 5). The same scale served for both, and by means of a system of mirrors the deflections of both were read simultaneously in the same telescope. The exciting source of the vibrator (induction coil or pliotron circuit) was controlled by strings passing through the wall. Thus all the observations could be made by one observer.

The energy emitted by the vibrator at any given instant was assumed to be proportional to the deflection of the galvanometer connected to *C*. The relative energy received at any point of the circle *D* was therefore proportional to the ratio of the deflection of *M* to the deflection of *C*. Several readings were taken for each setting of *M* and the average value

of M/C used. With increasing age of the vibrator the ratio M/C did not always remain constant, but generally decreased more or less irregularly. Consequently, frequent readings were taken with the main receiver in some chosen position on the circle D. If M/C varied the other readings were corrected, *i.e.*, the energy received at the various points along D was expressed in terms of the energy received at the reference position.

The possible sources of error in the present work are the following:

1. Effect of the box surrounding the prism.

2. Radiation penetrating the walls beyond the screen A.

3. Radiation reflected from the walls, floor and ceiling of the room in which the observations were made.

4. The disturbing influence of the induction coil and pliotron circuit.

The boards which formed the faces of the prism were quite uniform and free from knots. No disturbance could be expected from them. The only course of disturbance in the box was scattering by the bolts and screws at the vertical edges. The nearest that any of the bolts approached to the geometrical edge of the beam, measured from the edge of the screen B and in a place containing the axis of B, was 15°. If we substitute $\theta = 15°$, $\lambda = 7.8$ cm., $R = 25$ cm. in the formula

$$\text{Sin } \theta = \frac{m\lambda}{\pi R}$$

for the diffraction pattern, we find $m/\pi = .83$, which corresponds to the second maximum.[1]

Now the intensity of the second maximum is .017 times the intensity of the central maximum. Furthermore, not more than two of the bolts ever approached as close as 15° at one time, and all the screws were farther removed than the bolts. From this it appears that no appreciable error could have been introduced by the box surrounding the prism. To investigate this point further some observations were made with the frame removed. In this condition the prism rapidly lost its shape, but enough readings could be taken to show that the frame caused little trouble compared with the total effect observed.

The disturbance due to radiation penetrating the wall between the two rooms could readily be determined by noting the deflection of M when the aperture in A was closed by a screen. This was made very small by making A sufficiently large.

Although the room in which the observations were made was large (9.5 m. long, 8.5 m. wide, and 4 m. high), there was nevertheless an

[1] Wood's Physics Optics, p. 237.

appreciable disturbance due to reflection from the walls, etc., which could not be eliminated. Its magnitude was determined by making observations with a screen 85 cm. square interposed between the prism and M, near the former and perpendicular to the axis of the receiving mirror. The correction thus obtained included also (2) and to a certain extent (1). It was applied to all the observations made. If the vibrator was erratic, as was frequently the case toward the end of a series of observations, the readings for any given position of M were taken alternately with and without the screen. The average value of M/C with the screen was subtracted from the average value of M/C without the screen and the result taken as the true relative energy for that position of M.

The disturbance due to the exciting source consists of two parts: radiation from the leads to the vibrator and induced currents in the galvanometer leads. To determine whether radiation from the leads caused any trouble the vibrator was removed from its holder and the leads brought together making a spark-gap in air a few millimeters long. If this gap was much less than 3 mm. it was difficult to get rid of radiation. In all the work the side gaps in air between the leads and the vibrator were never less than 3 mm. In the case of the induction coil the radiation effect was eliminated by making the leads short and enclosing them in red fiber tubing. This material is a very poor dielectric at high frequencies and consequently helped to damp out the oscillations in the leads. The radiation effect in the case of the pliotron circuit was due to the oscillatory discharge of the condenser C, Fig. 3. This was readily eliminated by making the water resistance R sufficiently large.

As Sjöström[1] has observed, some receivers seem to be more sensitive to induced currents in the galvanometer leads than others. Trouble due to this cause was entirely confined to the check receiver when the pliotron circuit was used. By properly choosing the receiver and closely twisting the galvanometer leads it could be eliminated or at worst made very small.

After the apparatus was finally adjusted no disturbance due to the exciting source could be detected in the main receiver, while the effect on the check receiver, if it existed at all, was small and fairly constant. Since we are only interested in the relative values the inaccuracy introduced by a small constant error in the deflections of the check galvanometer is negligible.

RESULTS.

The energy distribution under various conditions is shown graphically in Figs. 6 and 7. The abscissæ are deviations in degrees measured from

[1] Loc. cit., p. 26.

the direction of the incident beam. The ordinates are energy expressed in per cent. of the maximum. With this system of coördinates the various curves are qualitatively comparable. The curves in Fig. 6 were taken with a vibrator consisting of .95 cm. spheres with an oil gap, excited by an induction coil. They confirm the theory qualitatively in that they show that some energy passes through the prism undeviated and that this effect decreases with increasing angle of incidence.

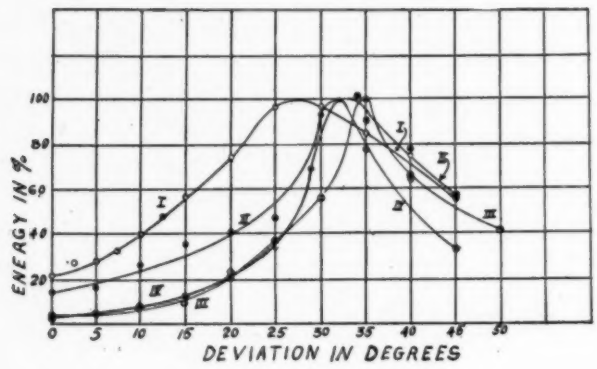

Fig. 6.

Spectral distribution of energy emitted by .95 cm. vibrator with oil gap.

I. Angle of incidence 0°
II. " " " 15°
III. " " " 24°
IV. " " " 32°

From curve IV., Fig. 6, it is seen that minimum deviation for the maximum in the energy curve occurs at 32° from which the index of refraction of pitch is found to be 1.99. This is much larger than the value 1.67 found by Hertz for waves about 60 cm. long.

Curves I. and II., Fig. 7, were obtained with a .95 cm. vibrator in air with the electric vector perpendicular to the refracting edge of the prism. They are much flatter than the corresponding ones for the oil gap and induction coil. This is due to the fact that the vibrator in air emits a more highly damped wave than in oil, so that a larger percentage of the total energy passes through the prism before the steady state is established. Figure 8 shows the variation of the energy which passes through the prism undeviated, with the angle of incidence. In this case the main receiver was kept fixed in the position of no deviation while the prism was rotated. The deflection of the main galvanometer for 0° incidence was 8.2 cm. and with the prism removed, 30.5 cm. With a screen interposed in the manner described the deflection was .2 cm.

Curve III., Fig. 7, shows the energy distribution for 32° incidence with a .95 cm. vibrator arranged so that the electric vector was parallel to

the refracting edge. It differs from II. in that it has a more distinct maximum. The undeviated energy was less than 2 per cent. of the incident energy as compared with 10 per cent. when the electric vector was perpendicular to the refracting edge. This is partly due to the difference in orientation of the receiver in the two cases. With the electric vector horizontal, *i.e.*, perpendicular to the refracting edge, the receiver was also horizontal and subtended an angle of about 6° at the axis of rotation of the prism. It was 20 cm. long and consequently energy brought to a focus a distance of 10 cm. on either side of the geometrical focus of the mirror was caught by the receiver. When the receiver was vertical it caught little energy except that which was brought

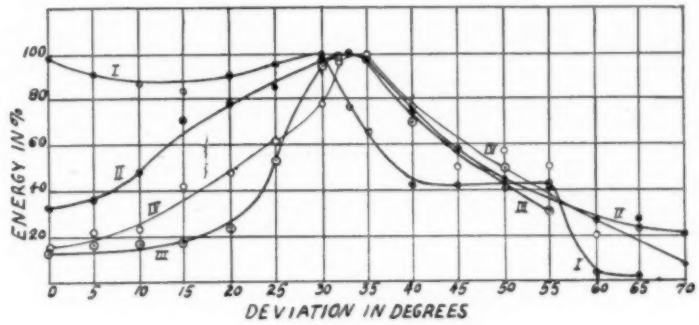

Fig. 7.

Distribution of energy emitted by vibrator with air gap.

I. Angle of incidence 0°, vibrator consisting of .95 cm. spheres.

II. Angle of incidence 32°, vibrator same as I.

III. Angle of incidence 32°, vibrator consisting of two .95 cm. spheres mounted with axis parallel to the refracting edge of the prism.

IV. Angle of incidence 32°, vibrator consisting of two 1.52 cm. spheres mounted with axis perpendicular to refracting edge of prism.

to a focus at the geometrical focus of the mirror. We should also expect a difference in the two cases in the direction observed since in the steady state the component of the electric vector in the plane of incidence is more readily transmitted than that perpendicular to the plane of incidence.

Curve IV., Fig. 7, shows the distribution of energy for 32° incidence using a 1.52 cm. vibrator in air mounted horizontally. The general shape of the curve is the same as in the corresponding case with the smaller vibrator. The deflections were very erratic beginning at 45° which accounts for the irregularities at 45° and 60°.

A few observations were made with a .61 cm. vibrator in air but the deflections were too small to be of much value. It does not seem feasible to use vibrators as small or smaller than this without some means of

increasing the energy emitted. This might be accomplished by enclosing the vibrator in a glass bulb either exhausted to a very low pressure or filled with some gas at a pressure of several atmospheres. In the latter case the decreased mobility of the ions would tend to set an upper limit to the useful frequency of the exciting source.

WAVE-LENGTH MEASUREMENTS.

The wave-length of the radiation emitted by the vibrator was measured by the Boltzmann mirror interference method first used by Klemenčič and Czermak.[1] In this method the energy from the vibrator arrives at the receiver after reflection from a mirror which is divided into two halves, so that the line of separation is in the plane of incidence. By separating the two mirrors thus formed, interference between the two halves of the beam takes place at the receiver. Each mirror consisted of a sheet of plate glass 35 cm. by 70 cm. covered with tinfoil, one was fixed and the other mounted on the carriage of a dividing engine. The wave-length is

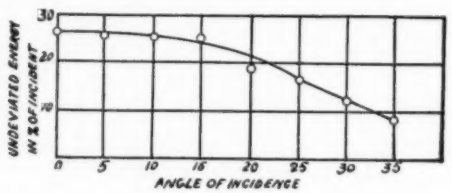

Fig. 8.

the distance between two successive maxima or two successive minima. For the .95 cm. spheres in air the wave-length was 7.8 cm. and for the 1.52 cm. spheres in air about 9 cm. In the latter case the maxima and minima of the interference curve were so flat that it was difficult to determine the wave-length accurately. These values indicate pronounced "mirror-action."[2]

The nature of this phenomenon is not very well understood. The size and shape of the collecting mirrors somehow influence the wave-length of the radiation. When the focal length is comparable to the wave-length the emitted beam has a more or less definite wave-length which is determined by the geometry of the mirror and not by the size of the vibrator. For the present purpose it is not essential that the vibrator emit its characteristic wave-length; all that it is desirable to know is what it actually does emit.

The theory indicates that the wave-length of the undeviated energy is very short and the intensity very weak compared with the incident

[1] Weid. Ann., 50, p. 177, 1893.

[2] Webb and Woodman, loc. cit., p. 100. These investigators found 6.7 cm. for the characteristic wave-length of a .95 cm. vibrator with an oil gap.

radiation. From this it appears that the effect observed is not due to strictly undeviated energy—*i.e.*, the disturbance called the "first forerunners" by Brillouin, but to energy that has undergone slight deviation. This view is strengthened by a consideration of the finite size of the receiver. An attempt was made to investigate the wave-length of the energy received in the neighborhood of zero deviation by means of the interferometer. No evidence of interference could be obtained. This was probably due to the fact that the energy reflected from the interferometer was not sufficiently monochromatic, since the wave-length depends upon the thickness of the medium traversed and consequently varies continuously from the refracting edge to the base.

The author takes pleasure in expressing his thanks to Dr. E. F. Nichols, who suggested the problem and method of solution, and to Professor L. Page, for advice concerning questions of theory. His thanks are also due Mr. G. C. Southworth, for advice on the construction and manipulation of the pliotron circuit.

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NOTE ON MUSICAL DRUMS.

BY R. N. GHOSH.

SYNOPSIS.

Vibration of Symmetrically Loaded Circular Membranes.—In India there are musical drums which are loaded over a central zone in such a way as to give harmonic partials. The *theory* is presented for two cases, namely when the load varies inversely as the first power and as the second power of the distance from the center. It is found that in the second case the partials form a harmonic series, whereas in the first case they do not.

IN India there are many musical drums like kettledrums which are used in company with stringed instruments. They differ from kettledrums in two respects, (1) they are loaded over a central zone; (2) they elicit harmonic partials.[1] It is well known that the partials of an unloaded circular membrane do not form a harmonic series, and a few of them give a consonant chord. From a look at the Indian instruments it becomes evident at once that the load per unit area varies as we proceed outward from the center. The investigation of the nature of the vibration when the load varies inversely (1) as the first power, and (2) as the second power of the distance from the center, can be effected very simply, but the writer could not find any mention of it in the textbooks.

The equation of motion in the case of circular membrane is given by

$$\rho \frac{d^2\omega}{dt^2} = T_1 \left\{ \frac{d^2\omega}{dr^2} + \frac{1}{r}\frac{d\omega}{dr} + \frac{1}{r^2}\frac{d^2\omega}{d\theta^2} \right\},$$

where the symbols have their usual meaning. Assume $\omega \propto \cos(kct)$ and

$$\rho = \frac{\rho_0}{r}. \tag{1}$$

Put $T_1/\rho_0 = c^2$ and further assume $\omega = v \cos(n\theta)$, then v must satisfy

$$\frac{d^2v}{dr^2} + \frac{1}{r}\frac{dv}{dr} + \left(\frac{k^2}{r} - \frac{n^2}{r^2}\right)v = 0. \tag{2}$$

Put $x = 2k\sqrt{r}$, then (2) becomes

$$\frac{d^2v}{dx^2} + \frac{1}{x}\frac{dv}{dx} + \left(1 - \frac{4n^2}{x^2}\right)v = 0. \tag{3}$$

$$\therefore \quad v = AJ_{2n}(x) = AJ_{2n}(2k\sqrt{r}).$$

[1] Nature, Jan. 15 (1920), p. 500.

If at $r = a$ the membrane is fixed we must have $J_{2n}(2k\sqrt{a}) = 0$ giving real values of k. The nature of these roots is well known, they do not from a harmonic series. The effect of the variation in density is mainly upon the absolute pitch of the vibrating membrane.

$$\text{Case II} \quad \rho = \frac{\rho_0}{r^2}. \tag{4}$$

Let us consider the simple case of symmetrical vibrations only, so that (2) becomes

$$\frac{d^2v}{dr^2} + \frac{1}{r}\frac{dv}{dr} + \frac{k^2}{r^2}v = 0. \tag{5}$$

$$\therefore \quad v = A \cos (k \log r). \tag{6}$$

The boundary condition gives

$$\cos (k \log a) = 0.$$

$$\therefore \quad k \log a = (2n + 1)\frac{\pi}{2}. \tag{7}$$

The partials now form a series of odd harmonics, and the absolute pitch is also disturbed.

MUIR CENTRAL COLLEGE,
ALLAHABAD, INDIA,
July, 21

ACOUSTIC WAVE FILTERS.

BY G. W. STEWART.

SYNOPSIS.

Acoustic Wave Filters Composed of a Series of Like Sections.—(1) *Theory.* Taking the impedance of any part of an acoustic circuit to be equal to the complex ratio of the applied pressure difference to the rate of change of volume displacement, it is shown that, neglecting dissipative forces, it is possible to construct a filter having limiting frequency values of no attenuation determined by the formulæ $Z_1/Z_2 = 0$ and $Z_1/Z_2' = -4$, where Z_1 is the impedance of the transmitting conduit circuit and Z_2 of each branch of each section. The impedance of any section depends on the inertance M of dimensions mass per unit area squared, and the capacitance C which has the dimensions of stiffness per unit area squared. If M and C are in parallel, $Z = iM\omega/(1 - MC\omega^2)$, whereas if they are in series, $Z = i(M\omega - 1/C\omega)$. For instance, in the case of a closed chamber or resonator, M and C are in series and are equal to ρ/C and $V/\rho a^2$ respectively where ρ is the density of the medium, c is the conductivity of the mouth, a the velocity of sound and V the volume. Formulæ are derived for various assumed cases. On account of the uncertainty as to whether a tube may be considered sa having the equivalent inertness and capacitance connected in parallel or in series, the application of these formulæ to actual cases is somewhat empirical. (2) *Construction and test of filters of three types.* Low-frequency-pass filters were made, for example, by two concentric cylinders joined by walls equally spaced and perpendicular to the axis. Each chamber thus formed had a row of apertures in the inner cylinder which served as the transmission tube. In one case the volume of each chamber was 6.5 cm.³, the radius of the inner tube 1.2 cm. the length between apertures, 1.6 cm. A chamber and one such length of the inner tube is called a section. Four such sections were found to transmit 90 per cent. of the sound from zero to approximately 3,200 d.v. where the attenuation became very high, resulting in zero transmission up to about 4,600 d.v. where transmission again appeared, Other similar filters of different dimensions attenuated through wider or narrower ranges. The lower limit of attenuation was found to correspond within 8 per cent. with the formula: $f = (1/\pi)(M_1C_2 + 4M_2C_2)^{-1/2}$. The upper limit was not predicted theoretically. High-frequency pass filters were made with a straight tube for transmission and short side tubes, for example, 0.5 cm. long and 0.28 cm. in diameter, opening through a hole with conductivity 0.08 into a tube 10 cm. long and 1 cm. in diameter. Six sections of such a filter would transmit about 90 per cent. of sounds above 800 but would refuse transmission to sounds of lower frequency. As would be expected, the cut off is not sharp. Filters with other dimensions were found to have an upper limit of attenuation varying from 450 to 2,300 d.v., agreeing with the formula $f = (1/2\pi)(1/4M_2C_1 + 1/M_1C_2)^{1/2}$, within about 13 per cent., on the average. The single-band filters made were a combination of the other two types, having side tubes leading to chambers of considerable volume. For instance, three sections each 5 cm. long and 0.5 cm. in diameter, with side tubes of the same size and 2.2 cm. long leading to a volume of 28 cm.³, transmitted between 270 and 370 d.v. The frequencies of the edges of the band of small attenuation are determined by the following formulae,

$$2\pi f = [M_2C_2(1 + M_2'/M_2)]^{-\frac{1}{2}} \text{ and}$$

$$2\pi f = [M_2C_2(1 + 4M_2/M_1)^{-1}(1 + M_2'/M_2 + 4M_2'/M_1)]^{-\frac{1}{2}}.$$ Such filters

exhibit the same variations from theoretical performance as would be expected from a combination of the other two types. However, the agreement of each type with theory is sufficient to enable filters to be designed to fulfill set conditions. The *attenuation secured* with only four sections is very great, the transmission being certainly less than 10^{-7} in the attenuated region, while it may rise to 90 per cent. in unattenuated regions. *Possible applications* of these simple filters in laboratory work and in connection with specking devices, are briefly suggested.

I. GENERAL INTRODUCTION.

THE selective transmission of an acoustic wave of a given frequency is well known. A Helmholtz resonator with a small ear opening is such a filter. Cylindrical tubes such as shown in Fig. 1 will also serve as filters, (*a*) transmitting chiefly the resonating frequencies of *cd* and (*b*) giving poor transmission especially for the resonating frequencies of *cd*. The acoustic wave filters which this article describes

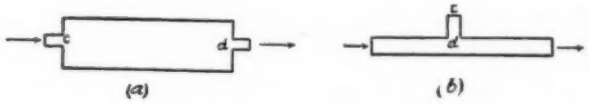

Fig. 1.

are different in principle and in performance in that they do not depend upon resonance itself, but upon the interaction between recurrent similar sections of a transmission "line," these sections containing the elements upon which free vibrations are to depend, and having over-all dimensions that are small in comparison with a wave-length of the sound.

These new filters are remarkable in that selected groups of frequencies, extending over a large range, can be eliminated in the transmission. Up to the present time, three kinds have been constructed and tested. The low frequency pass filter will give approximately zero transmission at all frequencies above, and a fairly good transmission below a certain predetermined frequency. The high-frequency filter will transmit above a minimum frequency. The single-band filter will transmit a group of frequencies. In all cases, the frequency limits are ascertained approximately by calculation from the dimensions so that the filters may be designed to fit specifications. In these filters, the cutoffs are not sharp and the performances are not exactly as just stated, but, as will be shown, the explanation is found in the fact that the experimental conditions only approximate the theoretical.

II. THEORY.

A. General.

An exact theoretical discussion of the acoustic wave filter may be possible, but certainly there is much to be gained in securing a theory

which, though only approximate, will aid in understanding the operation of the filters and in developing new designs. The well-known electric wave filters suggested to the writer the possibility of analogous effects in acoustics. Naturally, the theory[1] of the electric filters has been of much assistance.

Certain limitations will be imposed in our discussion. We will assume that the length of any selected section of an acoustic "line" or conductor is so small in comparison with a wave-length that no change in phase occurs therein. We will consider only sinusoidal waves. The term "acoustic impedance" will be used. Its absolute value is the ratio of the maximum pressure difference applied to the maximum rate of change of volume displacement. When complex notation is used for simplicity, as in alternating electric current theory, the acoustic impedance is the complex ratio of the pressure difference applied and the rate of change of volume displacement. The mathematical procedure will be based upon three hypotheses which are obviously reasonable approximations. They are: (1) the rate of volume displacement in any selected portion of the line, with a harmonically varying applied difference of pressure, can always be expressed by $Ie^{i\omega t}$ where I is complex; (2) the product of acoustic impedance and rate of volume displacement in any selected portion of the line equals the difference of pressure applied; (3) the algebraic sum of the volume displacements at any junction of lines is zero. By acoustic "line" is meant a bounded region of fluid or solid, forming a tube or channel and capable of transmitting sound waves in the direction of the tube or channel only.

We will consider an acoustic wave filter consisting of equal acoustic impedances in series, divided into sections by acoustic impedances in what might be termed shunt branches. In Fig. 2, let a sound wave of a

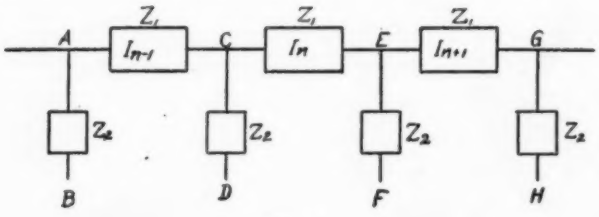

Fig. 2.

frequency $\omega/2\pi$ be transmitted through the line AG, a portion of an infinite line, containing a series of equal impedances, Z_1. Let each branch line AB, CD, EF, GH, etc., contain an impedance Z_2 and terminate in a

[1] U. S. Patent 1,227,113 by George A. Campbell. Chapter XVI. of Pierce's "Electrical Oscillations and Electric Waves," 1920.

volume of gas otherwise at rest, so that there is a common constant pressure at or near these termini. Let $I_n e^{i\omega t}$, etc., represent the rates of change of volume displacement in the corresponding lines, I_n being a complex quantity, and let the positive direction be from A to G. From the three conditions stated in the foregoing paragraph the following equation may be secured:

$$Z_2(I_{n-1} - I_n) = Z_2(I_n - I_{n+1}) + Z_1 I_n$$

or

$$I_{n+1} - \left(2 + \frac{Z_1}{Z_2}\right) I_n + I_{n-1} = 0. \tag{1}$$

This equation does not require an infinite line, but we will for convenience impose that condition. We may then write, using ΔP as the complex pressure difference over a branch,

$$\Delta P_{CD} = I_n(Z_1 + Z_\infty)$$

and

$$\Delta P_{EF} = I_{n+1}(Z_1 + Z_\infty),$$

wherein Z_∞ is the impedance of the infinite network to the right in the figure and has the same value in both equations.[1] Substituting the values,

$$\Delta P_{CD} = Z_2(I_{n-1} - I_n),$$
$$\Delta P_{EF} = Z_2(I_n - I_{n+1})$$

and dividing we have,

$$\frac{I_{n+1}}{I_n} = \frac{I_n - I_{n+1}}{I_{n-1} - I_n}$$

or

$$\frac{I_{n+1}}{I_n} = \frac{I_n}{I_{n-1}}. \tag{2}$$

Let us call the ratio of these successive I's, e^Y, where Y is unknown but in general is complex. Substitute in (1), and we have,

$$e^Y + e^{-Y} = 2 + \frac{Z_1}{Z_2}$$

or

$$\cosh Y = 1 + \tfrac{1}{2}\frac{Z_1}{Z_2}. \tag{3}$$

[1] The filter through its branches terminates in the undisturbed medium. The pressure at E can be expressed by $I_n Z_\infty$. From the equation of motion of a portion of a vibrating medium having a sinusoidal impressed force, and possessing mass, stiffness and dissipation, it can readily be shown that the impedance Z is a function of mass, stiffness, the dissipative factor and frequency only. In as much as these factors are the same for our Z_∞, whether taken from E or from G or any junction point, the assumption of identity of the Z_∞'s is justified.

If Y is a pure imaginary the rates of volume displacement in two adjacent sections differ only in phase. If Y is not a pure imaginary the rate of volume displacement is diminished in transmission, obviously the diminution occurring away from the input end. If Y is a pure imaginary, since $\cosh ix = \cos x$

$$+1 > \left(1 + \tfrac{1}{2}\frac{Z_1}{Z_2}\right) > -1 \tag{4}$$

and hence the limiting values of no attenuation are determined by the following:

$$\frac{Z_1}{Z_2} = 0, \tag{5}$$

$$\frac{Z_1}{Z_2} = -4. \tag{6}$$

We can find the limiting values of no attenuation in a filter by utilizing the actual values of Z_1 and Z_2. It would therefore appear that an acoustic wave filter can be constructed, the only uncertainty being the manner of constructing Z_1 and Z_2. In order to determine upon the practical development of the filter, idealized conditions will first be discussed.

B. Inertance and Capacitance in Parallel.

Consider two idealized diaphragms, a and b, supposed to move as a whole, the former having mass, m_a, and not stiffness, and the latter stiffness, f_b, and not mass. Let them have areas S_a and S_b and displacements ξ_a and ξ_b and let them be connected in parallel as branches of an acoustic line so that they are subject to the same fluid pressure differences, $Pe^{i\omega t}$. Then,

$$m_a\frac{d^2\xi}{dt^2} = S_aPe^{i\omega t} \qquad \text{and} \qquad f_b\xi_b = S_bPe^{i\omega t},$$

the latter being merely the definition of f_b.

If we are concerned with the total volume displacement of the gas at the diaphragms, X_a and X_b, these equations become:

$$\frac{m_a}{S_a^2}\frac{d^2X_a}{dt^2} = Pe^{i\omega t} \qquad \text{and} \qquad \frac{f_bX_b}{S_b^2} = Pe^{i\omega t}. \tag{7}$$

We wish to obtain an expression for dX/dt or the rate of change of volume displacement in the main line at the junction of these two branches. By integration we find,

$$\frac{m_a}{S_a^2}\frac{dX_a}{dt} = \frac{P}{i\omega}e^{i\omega t} \tag{8}$$

the constant of integration vanishing since we are dealing with a variation in dX/dt caused by P and vanishing with P. By differentiation we obtain,

$$\frac{f_b \frac{dX_b}{dt}}{S_b^2} = i\omega P e^{i\omega t}. \tag{9}$$

But we know that at the junction of the branches the algebraic sum of the rate of volume displacements must be zero, or

$$\frac{dX_a}{dt} + \frac{dX_b}{dt} = \frac{dX}{dt}. \tag{10}$$

Substituting the values of dX_a/dt and dX_b/dt just found, we obtain,

$$\frac{dX}{dt} = P e^{i\omega t}\left(\frac{1 - MC\omega^2}{iM\omega}\right), \tag{11}$$

wherein

$$M = \frac{m_a}{S_a^2} \quad \text{and} \quad \frac{1}{C} = \frac{f_b}{S_b^2}. \tag{12}$$

We will call M the *inertance*, C the *capacitance*, both defined by (12) and (7). We thus have for the impedance of the combination of the two circuits in parallel,

$$Z = \frac{iM\omega}{1 - MC\omega^2}. \tag{13}$$

Let us now assume that our impedances Z_1 and Z_2 are each composed of two such branches in parallel. The branch having mass, m_a, will vanish when $m_a = \infty$ or $M = \infty$ and the branch having stiffness, f_b, will vanish when $f_b = \infty$ or $C = 0$.

If we apply condition (5) to Z_1 and Z_2 as just determined in (13) and we have as a limiting frequency, f_1:

$$\omega^2 = \frac{1}{M_2 C_2} \quad \text{or} \quad f_1 = \frac{1}{2\pi}\sqrt{\frac{1}{M_2 C_2}}. \tag{14}$$

If we apply condition (6), we have:

$$\omega^2 = \frac{M_1 + 4M_2}{M_1 M_2(4C_1 + C_2)} \quad \text{or} \quad f_2 = \frac{1}{2\pi}\sqrt{\frac{M_1 + 4M_2}{M_1 M_2(4C_1 + C_2)}}. \tag{15}$$

In (14) and (15) the subscripts of M and C correspond to those adopted for the Z's. These frequencies f_1 and f_2 are those that limit the range in which there is no attenuation. It is to be observed that the range of no attenuation is one in which $\left(1 + \frac{1}{2}\frac{Z_1}{Z_2}\right)$ can change from $+1$ to -1.

But, from (13), Z_1/Z_2 is a continuous function of ω or $2\pi f$ and hence there is a continuous frequency range wherein there is no attenuation. A filter in which Z_1 and Z_2 each consists of an inertance and capacitance in parallel is thus possible.

C. Inertance and Capacitance in Series.

Consider each Z_1 and Z_2 to be an inertance and capacitance in series. The current must be the same throughout Z_1 or Z_2. Let P_1 be the pressure difference over the inertance, M_1, and P_2, over the capacitance, C_1. Then, from (7) and (8)

$$\frac{P_1}{i\omega M_1} = I = \frac{P_2}{\frac{1}{C_1 i\omega}}.$$

Hence

$$\frac{P_1 + P_2}{i\omega M_1 + \frac{1}{iC_1\omega}} = I$$

or

$$Z_1 = i\left(M_1\omega - \frac{1}{C_1\omega}\right). \tag{16}$$

If we now ascertain the limits of no attenuation, we have from (5),

$$f_1 = \frac{1}{2\pi}\sqrt{\frac{1}{M_1 C_1}} \tag{17}$$

and from (6)

$$f_2 = \frac{1}{2\pi}\sqrt{\frac{C_2 + 4C_1}{C_1 C_2(M_1 + 4M_2)}}. \tag{18}$$

Again we have the possibility of a filter.

A special and yet a common case of inertance and capacity in series is one wherein M_1 is the inertance of an orifice entering a chamber and C_1 is the capacitance of the chamber. The condition for resonance, or $Z = 0$, occurs as shown by (16) when,

$$M_1\omega = \frac{1}{C_1\omega} \quad \text{or} \quad f = \frac{1}{2\pi}\sqrt{\frac{1}{M_1 C_1}}. \tag{19}$$

But in orifices which are short compared with their diameters we cannot use for M_1 the mass divided by the square of the area, for this expression neglects the end effects of the channel. The well-known formula for the vibration of such a system is,[1] neglecting dissipation[2]

[1] Rayleigh, Theory of Sound, Vol. II., p. 195.

[2] Insertion of dissipation seems to lead to difficulties which are avoided by this approximation.

$$\frac{\rho}{c}\ddot{X} + \frac{\rho a^2}{V}X = Pe^{i\omega t} \tag{20}$$

from the solution of which we get,

$$\dot{X} = \frac{Pe^{i\omega t}}{i\rho\left(\frac{\omega}{c} - \frac{a^2}{V\omega}\right)}. \tag{21}$$

In these equations ρ is the density, c is the "conductivity" of the channel, a the velocity of sound and V the volume of the chamber.

It is evident that the new value of Z_1 viz.,

$$Z = i\rho\left(\frac{\omega}{c} - \frac{a^2}{V\omega}\right), \tag{22}$$

differs from (16) only by the apparent substitution of ρ/C for M_1 and $V/\rho a^2$ for C_1.

D. Inertance and Capacitance of a Tube.

In order to assist in constructing a filter, we will now discuss the nature of a column of gas, which we must use as Z_1 in our conducting line.[1]

Assume an acoustic plane simple harmonic wave passing along a tube in the direction of x. Let ξ be the displacement of a particle from its mean position; ρ the density, a the velocity of sound, and p the excess pressure over the mean.

Then

$$\rho\frac{\partial^2\xi}{\partial t^2} = -\frac{\partial p}{\partial x} \tag{23}$$

(an exact equation) and for small vibrations,[2]

$$\frac{\partial^2\xi}{\partial t^2} = a^2\frac{\partial^2\xi}{\partial x^2}. \tag{24}$$

From (23) and (24)

$$\rho a^2\frac{\partial^2\xi}{\partial x^2} = -\frac{\partial p}{\partial x}. \tag{25}$$

The integration of (25), since

$$\frac{\partial\xi}{\partial x} = 0$$

at all times when $p = 0$, gives

$$\rho a^2\frac{\partial\xi}{\partial x} = -p. \tag{26}$$

[1] Similar discussions occur in Drysdale, Jl. of Inst. Elec. Engs., July, 1920, Vol. 58, p. 591, and Kennelly and Kurowaka, Proc. Am. Acad., Feb., 1921, Vol. 56, No. 1, p. 29.

[2] Lamb's Hydrodynamics, 1916, p. 474.

We may write (26) as follows:

$$\rho a^2 \frac{\partial \xi}{\partial x} \frac{\Delta x}{\Delta x} = - p$$

and if we represent the volume in a length Δx by ∇V, we have,

$$\rho a^2 \frac{\Delta V}{V} = - p$$

or $\rho a^2 = - E$ where E is the modulus of elasticity of volume. Since the compression is due to p and not to changes of pressure along the line, the stiffness can be considered as analogous to stiffness in the walls of the tube upon which the pressure difference p acts. Our tube possesses inertance and capacitance as we know, but the above shows that these are not the equivalent of inertance and capacitance connected either in parallel or in series. Indeed, the capacitance can be thought of as between the inside and outside of the tube instead of along the tube.

Inasmuch as we must use tubes in a practical construction it is essential that we consider whether or not a tube can be used for either Z_1, or Z_2, arranged as in the preceding theory. Consideration shows that Z_1 cannot accurately be composed of a tube, for Z_1 is wholly in the line and not between the line and the outside. Hence we must ascertain whether or not such a substitution would be a sufficient approximation. In short, can we consider a tube as having the equivalent of inertance and capacitance connected in parallel or in series, or may we consider it as having inertance only or as capacitance only?

Assume that any tube we may use will be short as compared with a wave-length. Consider the gas to move as a whole. Then the δp is due to inertance. Or consider the gas to be stationary acting as a cushion. Then δp is due to capacitance. In both cases we have neglected the change of phase along the tube. Whichever case is the better approximation will depend upon the service the tube is rendering, or, in other words, will depend upon the adjacent construction or the composition of the filter. It might appear that the tube can be approximated by lumping the capacitance. This cannot be done at the center of the section for the general theory does not permit of a side branch other than Z_2. It cannot be lumped at Z_2 as can be shown by comparison of the resulting theory with experiment. The assumption of M_1 and C_1 in series does not appear reasonable for the total pressure over the section certainly acts on M_1. We are therefore forced to the policy of using M_1 and C_1 in parallel in the line with the understanding that experiment will determine empirically whether M_1 or C_1 or both shall be used in the

computations. As will subsequently be shown, experiments thus far seem to demand the introduction of C_1 in only one of the three types of filters. Thus the somewhat arbitrary manner of introducing C_1 in parallel is minimized. It is fair to say that, in this one case, the assumption seems not without a theoretical justification. It is thus observed that at the outset we are driven to an approximation which demands an empirical selection of formulæ.

III. Construction of Filters.

A. General Limitations.

If we are to construct an acoustic filter that will have good transmission we must avoid any changes in the nature of the medium and in the diameter of the transmitting conduit or conductor. If the filter is to have good attenuation, similar conditions would hold for the branch lines. For first experiments, then, a single medium and a transmitting line of constant cross section are chosen. These selections suggest, from the standpoint of convenience, the use of air and the use of a cylindrical tube as the boundary of the transmission line.

The only limitation to our application is that there be a series of like sections with Z_1 in the main line and Z_2 in the side branch. With no limitation placed upon the constitution of Z_1 or of Z_2, an infinite number of designs may be possible. But, as already stated, considerations lead to the selection of a cylindrical tube containing air as the transmission line. The impedance of a short section of such a line cannot be accurately expressed by an equivalent M_1 and C_1 connected either in series or parallel. We will assume M_1 and C_1 in parallel, for thereby we can make $M_1 = \infty$ or $C_1 = 0$ or remove them from consideration without obstructing the transmission of the line. But even with these limitations the number of filters is infinite, for Z_2 can be formed, theoretically, in any manner one chooses.

B. Low Frequency, High Frequency, and Single Band Pass Filters.

In order to determine the construction of low frequency and high frequency pass and single band filters in as simple a manner as possible, an additional provisional limitation will be made, viz., to filters in which Z_2 consists of an equivalent M_2 and C_2 connected either in series or parallel. We shall then have four quantities M_1, M_2, C_1 and C_2. If either M_1 or M_2 is absent, *i.e.*, removed from consideration, its value is infinity. Under similar conditions the value of a capacitance is zero. We have then to ascertain the possible combinations of

$$M_1 = \infty, \qquad M_2 = \infty, \qquad C_1 = 0, \qquad C_2 = 0.$$

Taken singly there are four combinations in pairs, six in triplets, four with one only, and one with none, making a total of fifteen possible combinations. If we remove those combinations which remove the *line* or the branches entirely, we have left nine designated as follows:

1. All present,
2. $M_1 = \infty$,
3. $M_2 = \infty$,
4. $C_1 = 0$,
5. $C_2 = 0$,
6. $M_1 = M_2 = \infty$,
7. $M_1 = \infty$, $C_2 = 0$,
8. $M_2 = \infty$, $C_1 = 0$,
9. $C_1 = 0$, $C_2 = 0$.

By the preceding, our values of acoustical impedances are limited to the following:

In the transmission line,

$$Z_1 = \frac{iM_1\omega}{1 - M_1C_1\omega^2}. \qquad (13) \text{ bis}$$

In the branch,

$$Z_2 = \frac{iM_2\omega}{1 - M_2C_2\omega^2} \qquad (13) \text{ tris}$$

or

$$Z_2 = i\left(M_2\omega - \frac{1}{C_2\omega}\right). \qquad (16) \text{ bis}$$

If the limits of no attenuation are now ascertained by the application of equations (5) and (6) we find the values in Table I. for the nine cases, each having the possibility of Z_2 in parallel or in series.

The explanation of most of the blanks in the fourth and fifth columns is that, assuming M_2 and C_2 to be in series, our original arrangement of Z_2 providing for the same pressure in common at the termini, requires the following:

1. There must always be an M_2 at the junction point, for otherwise there could be no $\dot{X}$ and hence no use of the side branch. Hence M_2 is at the junction point and C_2 is next in the branch.

2. M_2 cannot be infinity, for if infinity, the side branch would not be used at all.

3. C_2 cannot be zero for this would prevent any value of $\dot{X}$ and therefore any use of the side branch. Thus six of the nine cases are eliminated from consideration leaving only cases 1, 2 and 4. Case 1 leads to the possibility of an imaginary frequency and introduces two values of f_2,

TABLE I.

Case.	Parallel.		Series.	
	f_1.	f_2.	f_1.	f_2.
1	$\frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}}$	$\frac{1}{2\pi}\sqrt{\frac{M_1+4M_2}{M_1M_2(4C_1+C_2)}}$	0	
2	$\frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}}$	$\frac{1}{2\pi}\sqrt{\frac{1}{M_2(4C_1+C_2)}}$	∞	$\frac{1}{2\pi}\sqrt{\frac{C_2+4C_1}{4M_2C_1C_2}}$
3	0	$\frac{1}{2\pi}\sqrt{\frac{4}{M_1(4C_1+C_2)}}$		
4	$\frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}}$	$\frac{1}{2\pi}\sqrt{\frac{M_1+4M_2}{M_1M_2C_2}}$	0	$\frac{1}{2\pi}\sqrt{\frac{4}{C_2(M_1+4M_2)}}$
5	∞	$\frac{1}{2\pi}\sqrt{\frac{M_1+4M_2}{4M_1M_2C_2}}$		
6	0	0		
7	∞	$\frac{1}{2\pi}\sqrt{\frac{1}{4M_2C_1}}$		
8	0	$\frac{1}{2\pi}\sqrt{\frac{4}{M_1C_2}}$		
9	∞	∞		

which are not found in experience. Knowing that the assumption of C_1 in parallel with M_1 is arbitrary, we are justified in acknowledging the incorrectness of the assumption in this case and omitting the formulæ from consideration.

These considerations lead to the development of the three following types of filters:

1. Low-frequency pass filters; case 3, parallel; case 4, series; and case 8, parallel.

2. High-frequency pass filters; case 2, series; case 5, parallel; case 7, parallel.

3. Single-band pass filters; case 1, parallel; case 2, parallel; case 4, parallel.

Conditions of construction suggest that an additional formula for the single-band filter be determined. The three cases in which we have a

single-band filter as above stated, are those in which we have M_2 and C_2 in parallel. But in actual construction it is impractical to have truly a C_2 without an orifice into a volume and in this orifice we have an M_2' in series with C_2. A simple construction is thus suggested of taking *Case I* and adding an M_2' as an orifice into C_2. The impedance of the orifice and C_2 will be, according to (16)

$$Z_2' = i\left(M_2'\omega - \frac{1}{C_2\omega}\right).$$

This impedance is in parallel with the inertance M_2, the impedance of which is,

$$Z_2'' = i\omega M_2.$$

As readily follows from the definition of impedance and the fact that the sum of the two currents is the resultant branch current, the combined impedance, Z_2, is determined from the following relation,

$$\frac{1}{Z_2} = \frac{1}{iM_2\omega} + \frac{1}{i\left(M_2'\omega - \frac{1}{C_2\omega}\right)}$$

or

$$Z_2 = i\frac{M_2\omega\left(M_2'\omega - \frac{1}{C_2\omega}\right)}{M_2\omega + M_2'\omega - \frac{1}{C_2\omega}} = i\frac{M_2\omega(M_2'C_2\omega^2 - 1)}{M_2C_2\omega^2 + M_2'C_2\omega^2 - 1}. \quad (27)$$

According to equation (13) if we make C_1 arbitrarily zero for the sake of simplicity, we have

$$Z_1 = iM_1\omega. \quad (28)$$

If we now use the values of (27) and (28) for the conditions (5) and (6) we will have, respectively,

$$f_1 = \frac{1}{2\pi}\sqrt{\frac{1}{C_2(M_2 + M_2')}}, \quad (29)$$

$$f_2 = \frac{1}{2\pi}\sqrt{\frac{M_1 + 4M_2}{C_2(M_1M_2 + M_1M_2' + 4M_2M_2')}}. \quad (30)$$

C. Computation of Inertance and Capacity.

By comparison of (23) with (7) we see that the inertance for a straight tube, assumed to move as a whole, is,

$$M = \frac{m}{S^2} = \frac{\rho lS}{S^2} = \rho\frac{l}{S}. \quad (31)$$

In the case of an orifice, M, as already shown, is expressed by ρ/c where c is the conductivity. The expression for c in terms of the radius, R, and length, l, of the channel is[1]

$$c = \frac{\pi R^2}{l + \frac{\pi R}{2}}. \tag{32}$$

With l large in comparison with $\pi R/2$, this reduces to S/l and $M = \rho(l/S)$ as already stated.

As shown in the discussion of (22) we should substitute $V/\rho a^2$ for C_1. Therefore our equations for substitution are:

$$M = \frac{\rho}{c} = \frac{\rho\left(l + \frac{\pi R}{2}\right)}{\pi R^2} \tag{33}$$

and

$$C = \frac{V}{\rho a^2}. \tag{34}$$

D. Form of the Filters.

(*a*) *Low-Frequency Pass Filter.*—In a preceding section we found at least three formulæ for a low-frequency pass filter. They are as follows:

$$f_1 = 0, \qquad f_2 = \frac{1}{\pi}\sqrt{\frac{1}{M_1(4C_1 + C_2)}} = \frac{1}{\pi}\sqrt{\frac{1}{M_1C_2 + 4M_1C_1}}, \tag{A}$$

requiring that C_2 be the only portion of the branch;

$$f_1 = 0, \qquad f_2 = \frac{1}{\pi}\sqrt{\frac{1}{C_2(M_1 + 4M_2)}} = \frac{1}{\pi}\sqrt{\frac{1}{M_1C_2 + 4M_2C_2}}, \tag{B}$$

requiring that M_2 and C_2 be connected in series and that C_1 be zero;

$$f_1 = 0, \qquad f_2 = \frac{1}{\pi}\sqrt{\frac{1}{M_1C_2}}, \tag{C}$$

requiring that C_2 be the only portion of the branch and that C_1 be zero.

All these formulas are dimensionally correct and there is no conclusive evidence showing that one is superior to another save by actual experiment. Attention may be called, however, to the difficulty of constructing a C_2 without an M_2 in series. With C_2 only the most favorable cross-section of construction would be similar to Fig. 3. But there would be an M_2 and the justification for neglecting it would be raised.

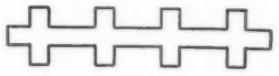

Fig. 3.

[1] Rayleigh, Theory of Sound, Vol. II., p. 181.

If the construction is made as in Fig. 4, the M_2 is better defined and can be determined from equation (33). These considerations point to the use of (*B*).

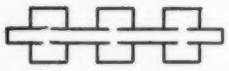

Fig 4.

(*b*) *High-Frequency Pass Filter.* — We previously found three simple cases of a high-frequency pass filter. The formulæ are as follows:

$$f_1 = \infty, \qquad f_2 = \frac{1}{2\pi}\sqrt{\frac{C_2 + 4C_1}{4M_2C_1C_2}} = \frac{1}{2\pi} = \sqrt{\frac{1}{4M_2C_1} + \frac{1}{MC_{22}}} \qquad (D)$$

requiring that $M_1 = \infty$;

$$f_1 = \infty, \qquad f_2 = \frac{1}{2\pi}\sqrt{\frac{M_1 + 4M_2}{4M_1M_2C_1}} = \frac{1}{2\pi}\sqrt{\frac{1}{4M_2C_1} + \frac{1}{M_1C_2}} \qquad (E)$$

requiring that $C_2 = 0$;

$$f_1 = \infty, \qquad f_2 = \frac{1}{2\pi}\sqrt{\frac{1}{4M_2C_1}}, \qquad (F)$$

requiring that $M_1 = \infty$ and $C_2 = 0$. Formula (*E*) and (*F*) indicate that it might be possible to construct such a filter with a straight tube and side branches consisting of M_2 only, or consisting of orifices. This plan has been followed in the filters herein described.

(*c*) *Single-Band Filter.*—We previously found four simple single-band filters. The formulæ are as follows:

$$f_1 = \frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}}, \qquad f_2 = \frac{1}{2\pi}\sqrt{\frac{M_1 + 4M_2}{M_1M_2(4C_1 + C_2)}}$$

$$= \frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}\left[\frac{1 + 4\dfrac{M_2}{M_1}}{1 + 4\dfrac{C_1}{C_2}}\right]}, \qquad (H)$$

requiring that all of the four elements remain in consideration;

$$f_1 = \frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}}, \qquad f_2 = \frac{1}{2\pi}\sqrt{\frac{1}{M_2(4C_1 + C_2)}}$$

$$= \frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}\left[\frac{1}{1 + 4\dfrac{C_1}{C_2}}\right]}, \qquad (I)$$

requiring that $M_1 = \infty$;

$$f_1 = \frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}}, \qquad f_2 = \frac{1}{2\pi}\sqrt{\frac{M_1 + 4M_2}{4M_1M_2C_2}}$$

$$= \frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}\left[\frac{1}{4} + \frac{4M_2}{M_1}\right]}, \qquad (J)$$

requiring that $C_1 = 0$. The fourth pair of values requiring that $C_1 = 0$ is found in equations (29) and (30) or

$$f_1 = \frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}\left[\frac{1}{1+\frac{M_2'}{M_2}}\right]}, \quad f_2 = \frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}\left[\frac{1+4\frac{M_2}{M_1}}{1+\frac{M_2'}{M_2}+\frac{4M_2'}{M_1}}\right]}. \quad (K)$$

E. Empirical Character of Formulæ.

We are prevented from securing accurate formulæ by the following circumstances:

1. Our dimensions cannot be vanishingly small as compared to a wave-length and therefore appreciable phase differences occur in any section or branch.

2. We cannot get an accurate expression for the impedance of a short tube because our theory assumes that this impedance is strictly in the line, whereas a tube has distributed capacitance virtually between itself and the undisturbed surrounding medium.

3. One hypothesis upon which the theory is based assumes that the junction points are really points, *i.e.*, there can be no accumulation there.

In respect to these circumstances stated, it is fair to say that the accuracy of the approximations cannot be estimated save by experiment. It is allowable, therefore, to take the position that we are to seek, in the case of each construction, that pair of formulæ which seems best to agree with experiment. In other words, the formulæ are somewhat empirical, though their manner of derivation gives a reason for their forms. This attitude of empiricism does not, then, hide the nature of the phenomena but rather decides as to the best approximation.

IV. Comparison of Theory and Experiment.

A. Measurement of Transmission.

An apparatus, Fig. 5, similar to that used by Drs. Gray and Roebuck, but not described in print, gave sufficiently accurate measurements of

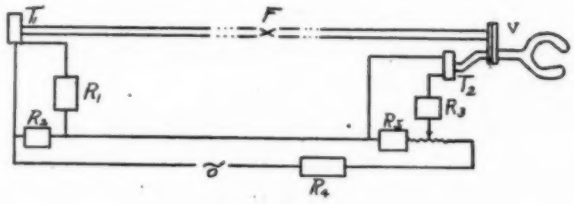

Fig. 5.

the transmission of the filters. T_1 and T_2 are similar telephone receivrse, V is a valve connecting a pair of stethoscope binaurals to either T_2 or

the tube which connects to the filter F and T_1, the resistance boxes are marked by the R's, and the source of sinusoidal currents is an oscillator loaned by the Western Electric Company. The circuits of the latter consist of an oscillating circuit, an amplifier, an electrical low-frequency pass filter of two sections, a resistance R_4, and inductances and capacities by means of which it was possible to get fairly pure tones from 90 to 1,500 vibrations and tones up to 5,000 without the use of a filter. R_2 was small in comparison with R_1 and the latter about ten times the impedance of T_1 for a frequency of 1,000 cycles. R_5 was never greater than one tenth the impedance of T_2 and R_3. The brass tubing on either side of F was .557 cm. in internal diameter and 2.5 meters long. The method pursued was to adjust the values of the R's so that, without the acoustic filter present, the values of R_5 required to produce the same intensity at the stethoscope with either acoustic connection, were not in excess of the limit above stated. Each filter had its conducting tube of approximately the same diameter as the tubes from F_1 to T_1 and V. Settings of R_5 were recorded for the various frequencies with and without F, in the latter case a tube of the same length and internal diameter being substituted for F. The transmitted intensities were assumed proportional to the square of R_5. Thus the percentage transmission of F at a certain frequency would be the ratio between the squares of R_5 with F and with its substitute tube. Obviously, the tubes in the apparatus have resonance and this will greatly reduce the accuracy of the transmission values. For frequencies lower than 2,000, pieces of hair felt were inserted every 15 cm. or so to increase the viscosity and reduce resonance. Improved readings were then obtained. The curves herewith presented must be examined with the understanding that resonance does exist. Since our immediate object was merely to get an estimate of the filtering action rather than an accurate measure of transmission, no effort at further refinement was considered. Experiments showed that even with the felt present, variations of 10 per cent. to 20 per cent. apparent transmission with frequency might occur.

B. Low-Frequency Pass Filters.

The general construction of the low-frequency pass filters and the experimental transmission curve is shown in Fig. 6. The accompanying Table II. gives the dimensions, the computations and certain experimental facts concerning a number of low-frequency filters. In this Table l, r, and V refer to the length of section, internal radius and volume respectively. The subscript 1 refers to the conducting line or tube and the subscript 2 to the branches or in the case of the form here used, to

the surrounding tube. The value f_m is the value of the frequency at which the transmission is 50 per cent. of the "unattenuated" transmission of the filter. Inasmuch as the beginning of attenuation cannot be sharp, this mean value is perhaps the fairest selection of an experimental value. The computations indicated by the letters, A, B, and C were made according to the formulæ so marked in the preceding theory. These formulæ when expressed in terms of the dimensions become, after

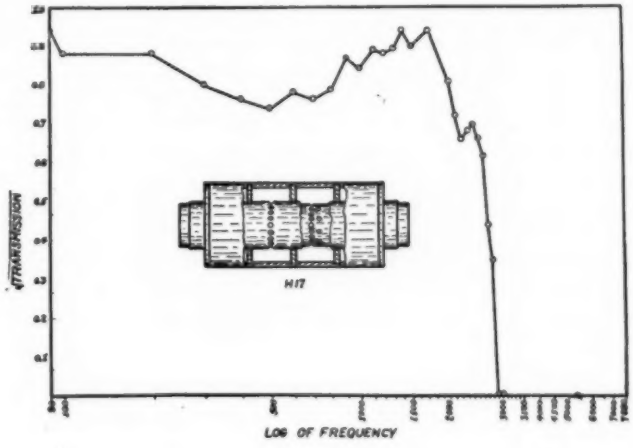

Fig. 6.

substitution in accord with (31), (33) and (34), respectively, (A'), (B') and (C') as follows:

$$f_1 = 0, \qquad f_2 = \frac{a}{\pi}\sqrt{\frac{S_1}{l_1 V_2}\left[\frac{1}{1 + 4\dfrac{l_1 S_1}{V_2}}\right]}, \tag{A'}$$

$$f_1 = 0, \qquad f_2 = \frac{a}{\pi}\sqrt{\frac{S_1}{l_1 V_2}\left[\frac{1}{1 + 4\dfrac{S_1}{c l_1}}\right]}, \tag{B'}$$

$$f_1 = 0, \qquad f_2 = \frac{a}{\pi}\sqrt{\frac{S_1}{l_1 V_2}}. \tag{C'}$$

It is evident that the formula (B') is to be preferred since it gives approximately the experimental values of f_m and also explains satisfactorily the variation of the frequency limit of attenuation with the conductivity of the orifices leading from the transmission conduit to the volume in the branch.

Attention should be directed to several other facts shown in the table. The percentage transmission in the "unattenuated" region given in column "T," seems to depend upon the ratio between r_2 and r_1, the

TABLE II.

No.	No. of Sections.	l_1 cm.	r_1 cm.	r_2 cm.	V_{s_2} cm.	f_m d.v.	$f_2(A')$ d.v.	$f_2(B')$ d.v.	$f_2(C')$ d.v.	No. of Apertures.	T %.	*Faf*	
												f	%.
2	3	2.66	.243	1.71	21.6	450	595	462	624	2	.20	5,250	708
3	5	5.0	.243	1.71	43.1	230	308	291	321	4	.36	3,100	933
13	4	4.0	1.42	2.57	44.4	920	1,140	880	2,075	6	.80	3,300	106
15	4	1.67	.75	1.42	5.94	2,200	2,670	2,710	4,620	16	.80	5,150	106
15	4	1.67	.75	1.42	5.94	1,700	2,670	2,120	4,620	8		2,900	38
16	4	1.67	.75	1.15	2.62	3,200	2,965	4,085	6,960	16		6,200	55
16	4	1.67	.75	1.15	2.62	2,500	2,965	3,200	6,960	8		4,000	29
17	4	1.67	.75	1.30	4.36	2,700	2,800	3,175	5,400	16	.65	5,200	66
17	4	1.67	.75	1.30	4.36	2,200	2,800	2,480	5,400	8		3,000	25
*R*1	3	1.58	1.19	1.82	7.1	2,700	3,080	2,840	6,885	8	.90	3,500	9.4
*R*2	4	1.58	1.19	1.82	7.1	2,750	3,080	2,840	6,885	8	.72	4,000	25
*R*3	4	1.32	1.19	1.82	5.87	3,350	3,700	3,170	8,300	8	.72	4,750	18.7
*R*4	4	1.45	1.19	1.82	6.48	3,025	3,370	3,010	7,520	8	.90	4,600	65
*R*5	6	2.58	1.19	1.82	11.82	2,000	1,890	2,095	4,180	8	.90	3,000	25
*R*6	6	1.58	1.19	1.82	7.1	2,700	3,080	2,700	6,885	4	.90	4,750	44
*R*6	6	1.58	1.19	1.82	7.1	2,075	3,080	2,100	6,885	4	.72	3,100	24

number of sections constant, the greater the ratio the less the transmission. In the last two columns labeled "*Faf*," the one under "f" refers to the first audible frequency above the cut-off, and under "%" the ratio between the range of inaudibility and the actual cut-off. Here we note that while filters in which r_2/r_1 is large have inferior transmission, yet they have a surprisingly great range of frequencies above the cut-off where the filter operates successfully. In filters 2 and 3 this range is at least over ten times the cut-off frequency. As the ratio of r_2/r_1 becomes smaller, this cut-off range decreases but the transmission in the "unattenuated" region improves. It is impossible to select, without specifications and trial, the most successful design for a given frequency cut-off, for success depends upon both the range of cut-off and upon the percentage of transmission in the unattenuated region desired. The remarkable feature is that the high attenuation in the region above the theoretical lower limit, f_2, is ever as great as ten times this limit. In fact, in the case of No. 2, that frequency having a wave-length of approximately the length of a section is highly attenuated. The performance is better than one would hope. Attention is directed to *R* 1, a tube about 6 cm. long and 2.4 cm. in diameter yet capable of having an attenuation producing inaudible transmission for a considerable range above the cut-off. Such a performance is a surprise to one accustomed to the difficulty in preventing the passage of sound through holes and channels.

C. *High-Frequency Pass Filters.*

We previously have mentioned three possible simple cases of a high-frequency pass filter but two of these seemed to consist merely of a straight tube with side branches each having an M_2 or orifices, only. The cross-section of such a filter and its transmission is shown in Fig. 7.

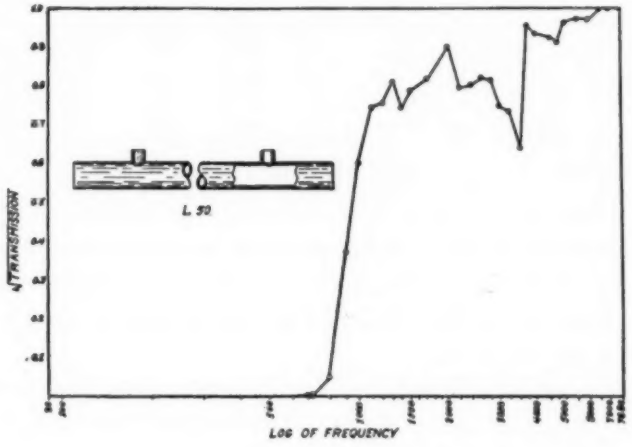

Fig. 7.

If we substitute in the formulæ, (E) and (F) in accord with (33) and (34), we obtain the following:

$$f_1 = \infty, \qquad f_2 = \frac{a}{2\pi}\sqrt{\frac{c}{4V_1}\left(1 + \frac{4S_1}{l_1 c}\right)}, \tag{E'}$$

$$f_1 = \infty, \qquad f_2 = \frac{a}{2\pi}\sqrt{\frac{c}{4V_1}}, \tag{F'}$$

wherein c is the conductivity of the orifice as defined in (32).

Data of several filters of differing dimensions are given in Table III. The last column found in Table II. is here omitted because these filters gave transmission up to the highest frequency tried—5,000–7,000 d.v. The experimental results are therefore strictly in accord with the limits of attenuation set by the theory from f_2 to zero. A reason is doubtless that the less the frequency the more nearly the experimental conditions meet those assumed in the theory.

The general conclusion is that the formula (E') is very satisfactory. It is to be noted that in (E) we have used C_1. This is the only case of the three where experiment has indicated that C_1 should be used. As stated in the discussion of the theory, the assumption of C_1 in parallel with M_1 is arbitrary. A justification may now be seen in the following fact. The branch lines, M_2, are short. Thus there is a much greater

TABLE III.

No.	No. of Sections.	l_1 cm.	r_1 cm.	l_2 cm.	r_2 cm.	c.	f_m.	$f_2(E')$.	$f_2(F')$.	T.
15 II....	8	2.5	.243	0.5	.115	.061	2,300	2,400	988	.75
19.....	4	5.0	.243	0.5	.115	.061	1,500	1,300	699	.60
22.....	8	2.5	.243	0.5	.152	.099	2,200	2,520	1,262	.50
1,2,3,4..	8	4.0	.483	1.22	.278	.146	1,500	1,490	610	.75
50.....	12	5.0	.483	0.5	.139	.0845	920	1,170	415	.85
50.....	6	10.0	.483	0.5	.139	.0845	810	620	293	.90
50.....	4	15.0	.483	0.5	.139	.0845	525	436	240	.90
50.....	3	20.0	.483	0.5	.139	.0845	450	344	207	.90

pressure gradient in M_2 than in the conduit or conducting line itself. The particle velocity in M_2 is therefore much greater than in the conduit. If the particle velocity in the line were actually at rest, the conduit would serve as a capacitance for M_2. Thus, the existence of an effective capacitance is not surprising.

Attention should be called to the fact that experiment showed that as M_2 was made longer or very narrow, introducing viscosity, the cut-off became less sharp.

D. Single-Band Filters.

We have already presented four pairs of formulæ for single-band filters. If we now have a filter of the construction shown in Fig. 8 and denote

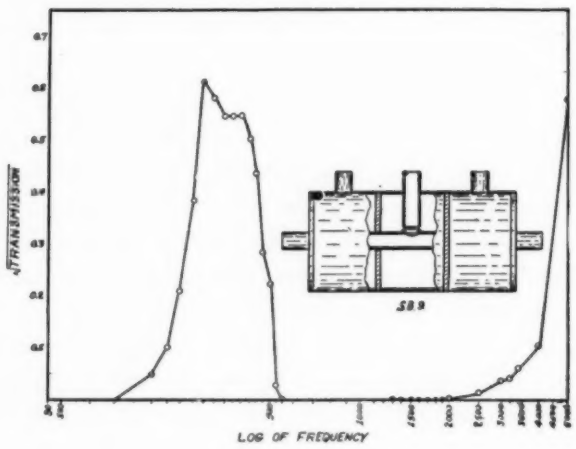

Fig. 8.

by l_2, S_2 the length and area of the side tube and by c the conductivity of the holes from the side branch into the chamber V_2, these four formulæ

may be written after substitution according to (33) and (34) as follows:

$$f_1 = \frac{a}{2\pi}\sqrt{\frac{S_2}{l_2 V_2}}, \qquad f_2 = \frac{a}{2\pi}\sqrt{\frac{S_2}{l_2 V_2}\left[\frac{1 + 4\frac{l_2 S_1}{l_1 S_2}}{1 + 4\frac{l_1 S_1}{V_2}}\right]}, \qquad (H')$$

$$f_1 = \frac{a}{2\pi}\sqrt{\frac{S_2}{l_2 V_2}}, \qquad f_2 = \frac{a}{2\pi}\sqrt{\frac{S_2}{l_2 V_2}\left[\frac{1}{1 + 4\frac{l_1 S_1}{V_2}}\right]}, \qquad (I')$$

$$f_1 = \frac{a}{2\pi}\sqrt{\frac{S_2}{l_2 V_2}}, \qquad f_2 = \frac{a}{2\pi}\sqrt{\frac{S_2}{l_2 V_2}\left(1 + 4\frac{l_2 S_1}{l_1 S_2}\right)}, \qquad (J')$$

$$f_1 = \frac{a}{2\pi}\sqrt{\frac{cS_2}{V_2(l_2 c + S_2)}}, \qquad f_2 = \frac{a}{2\pi}\sqrt{\frac{S_2}{l_2 V_2}\left[\frac{1 + 4\frac{l_2 S_1}{l_1 S_2}}{1 + \frac{S_2}{l_2 c} + \frac{4S_1}{c l_1}}\right]}. \qquad (K')$$

Fig. 8 also shows the transmission curve of one of the filters, SB_9, with which the range of highly attenuated frequencies above f_2 is relatively small. The two-column "*Faf*" in Table IV. is similar to that in Table II. The reasons for the lack of attenuation in these high frequencies are doubtless the same as in the case of the low-frequency pass filters described in a previous section. For, as will be observed, the single-band filter may be looked upon as a combination of the two other types. The experimental results show the (K') formulæ to be the most satisfactory.

V. Discussion and Conclusions.

The high attenuation secured with but few sections was not anticipated. General experience in acoustics increases the remarkableness of the action of the filters. The agreement with the theory is, in view of the assumptions made, fairly satisfactory for it is possible to construct filters that meet specifications.

The physical action considered herein is clearly not dissipation but interference. With a source transmitting energy through a filter, the action of the latter is to prevent the emission of energy from the source in these frequencies for which there is attenuation. There is dissipation, or at least a decrease in transmission in the filters, extending over the unattenuated region and this seems to be the greater, in the case of the low-frequency-pass filter, the greater the ratio of r_2 and r_1.

The extent of the usefulness of the filter will be determined by experience. Its simplicity and cheapness of construction make it a serviceable

TABLE IV.

No.	No. of Sections.	l_1 cm.	r_1 cm.	l_2 cm.	r_2 cm.	V_2 cm.^{3}	c	Observed.		Computed.						T %.	Faf	
								f_1	f_2	$f_1(H'I'J')$	$f_2(H')$	$f_2(I')$	$f_2(J')$	$f_1(K')$	$f_2(K')$			%.
1	3	5.0	.243	2.33	.243	42.7	0.69	190	260	236	380	227	400	224	346	.12	3,000	900
2	3	2.66	.243	2.33	.243	21.19	0.69	275	375	304	680	322	710	318	575	.26	3,000	500
3	3	5.0	.243	2.20	.243	28.02	0.69	270	370	300	468	282	499	283	430	.23	2,200	389
4	3	2.66	.243	1.70	.243	14.81	0.69	430	520	470	830	441	882	436	707	.28	3,125	400
5	3	5.0	.243	3.35	.243	28.02	0.69	190	270	242	439	228	466	234	410	.28	2,100	425
6	3	2.66	.243	2.80	.243	14.81	0.69	350	500	366	782	344	835	349	680	.29	3,000	400
7	3	1.17	.243	1.20	.243	5.74	0.69	700	1,300	836	1,875	835	2,030	810	1,380	.54	3,200	129
9	3	2.66	.243	2.40	.243	22.7	.455	285	475	319	648	306	685	295	506	.37	1,300	106
10	4	1.77	1.12	0.5	.278	14.4	.58	600	1,250	1,407	2,255	960	3,590	1,080	1,530	.56	1,800	33

device. In the laboratory it can be used in the elimination of undesirable components in a sound wave, and for certain types of sound analysis. In the latter case its advantage over a resonating device is its selection of a band of adjustable width. Its possible fields of usefulness in practical instruments may be merely mentioned. In the rendition of records on the phonograph and in the wireless telephone many undesirable frequencies can be removed. In wireless telegraphy an acoustic filter makes possible the simultaneous reception of an indefinite number of messages with the same antenna. In connection with a megaphone on a loud-speaking device, the filter has also an application. The introduction of this new filtering phenomenon may in time affect the design of musical instruments. Although the future use of the acoustic filter cannot be foreseen, there is one fundamental fact to be recognized, namely, that an aerial wave is used in audition and that a modification of this wave by a strictly acoustical method wherein the air is the medium, gives an opportunity for the energy to flow directly from the filter to the ear without any transformation which would introduce undesirable modifications. These acoustic filters have a great acoustic interest and the investigation of them, both theoretical and experimental, is being continued.

PHYSICAL LABORATORY,
STATE UNIVERSITY OF IOWA.

A STUDY OF THE EXCITING POWER FOR FLUORESCENCE OF THE DIFFERENT PARTS OF THE ULTRAVIOLET SPECTRUM.

BY LELAND JAYNES BOARDMAN.

SYNOPSIS.

Intensity of Fluorescence as a Function of Wave-length of Exciting Light, 0.55 to 0.2 μ.—The purpose of the experiment was to determine what wave-lengths are effective in excitation and what relations exist between these wave-lengths and the corresponding absorption and fluorescence spectra. Light from a source giving a continuous spectrum was dispersed by means of a quartz spectrograph and allowed to fall on the substance to be studied which was spread on a flat surface. Then the parts of the spectrum which excited fluorescence were observed or photographed by means of the fluorescent light. *A preliminary study of seventy substances* showed that all the oxides (20) and simple chlorides (8) tested were not excited, a few substances (7) including zinc silicate, zinc sulphate and cadmium phosphate fluoresced faintly, a few responded well (anthracene, eosin, fluorescein, phenolphthalein, calcium tungstate, and phosphorescent willemite), while the uranyl compounds (20) fluoresced strongly. For the last group the effective spectrum extended from 0.55 to 0.35 μ only, while for the others it extended continuously to 0.2 μ except in the case of four substances for which light from 0.35 to 0.325 was ineffective. *Excitation band spectrum for twelve uranyl compounds* was determined by measuring the density of the plates as a function of the wave-length by means of a sensitive photoelectric spectrophotometer. Some curves are reproduced and the wave-numbers corresponding to from 35 to 105 maxima for each compound are given. *Comparison with absorption spectra* shows close agreement, an absorption band corresponding to an excitation band in every case. This relation had previously been found by Howe to hold for phosphorescent sulphides.

Absorption Spectrum of Twelve Uranyl Compounds, from 0.55 to 0.32 μ.—Because of the correspondence noted above the excitation bands may be taken to be absorption bands and thus the known absorption spectrum be considerably extended toward both the red and ultraviolet. Comparison of these bands with the fluorescence spectrum indicates clearly many new reversing regions where the fluorescent light obscures the absorbing effect. These are listed.

INTRODUCTION.

THE purpose of this investigation is to study the behavior of different portions of the ultraviolet spectrum as regards the ability of exciting fluorescence. The major part of previous work in fluorescence has been confined to a study of the fluorescence and absorption spectra of various materials and the relations between the two. This enables one to describe the phenomena, or state what happens as the result of the mechanism producing fluorescence. It also throws some light on the nature of the mechanism itself.

It seemed probable that something could also be learned about this mechanism by studying the means by which it is set in operation: in other words by studying the conditions and means by which fluorescence is excited. As a part of this problem it is of interest to determine what wave-lengths are effective in excitation and what relations exist between the excitation, absorption, and the fluorescence spectra. Almost the only work that has been done along this line is that of Stokes,[1] and, for a certain group of materials, the work of Lenard.[2]

The method of the present investigation is similar to that used by Stokes. Quartz was however used in place of glass, and better sources of ultraviolet light were employed. Fig. 1 shows the arrangement of the apparatus. Light from the source *S* passed through a spectrograph, and then fell upon the fluorescent substance mounted in the plane of the plate-holder of the spectrograph at *A*.

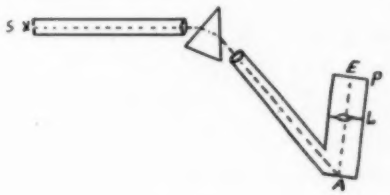

Fig. 1.

With the room darkened the fluorescence was studied for color and relative intensity by the eye at *E*. For more accurate study a photograph was taken by means of a camera lens *L* and a plate at *P*. In this way the exciting power of any region of the ultraviolet light was easily determined, since the dispersed light fell immediately upon the specimen spread out to intercept the entire beam of light.

It was necessary to use a light source which gives a continuous ultraviolet spectrum as free as possible from lines or bands. An electric spark under water was quite satisfactory for a large range of the ultraviolet spectrum. Other sources of light could be used to better advantage however in the visible and near ultraviolet region, since it was very difficult to maintain a spark in water for a sufficiently long time to give a proper exposure for the regions of weak fluorescence. Some photographs were however obtained by long excitation by the spark. By the method of producing the under-water spark used in this work, which is described in another paper soon to be published, it was possible to maintain a vigorous spark discharge 8 mm. in length for half an hour in distilled water, by means of a Tesla coil operated by a transformer of one kilowatt capacity.

It was found that a 400 c.p. nitrogen-filled glass-bulb Mazda lamp gave sufficient intensity in the near ultraviolet, and this was used when

[1] Stokes, Phil. Trans., p. 463, 1852.

[2] Lenard, P. Ueber Lichtemission und deren Erregung. Annalen der Physik, 31, p. 641, 1910.

possible because of its greater convenience. For somewhat shorter wavelengths a similar lamp with a quartz bulb was used.

Two spectrographs were used: the Fuess type, which gives a spectrum about 5 cm. long, range 580 $m\mu$ to 200 $m\mu$, and a Hilger instrument which gives five regions (5 settings) of the spectrum with a total length of about 30 cm., range 800 $m\mu$ to 205 $m\mu$. This spectrograph, which proved to be excellent for the purpose, is constructed so that five adjustments of its parts can be made for each of the five ranges or parts of the spectrum. The ranges are: 800 to 400 $m\mu$, 400 to 305, 305 to 255, 255 to 225 and 225 to 205. The five adjustments are: position of collimating lens, angle at which the prism is set, the angular position of the arm carrying the plate-holder, the position of the objective lens, and the angle which the plane of the plate-holder makes with the axis of the plate-holder arm. The data furnished by the makers for the various adjustments were corrected for this particular instrument and plotted in such a way as to show the relation between each variable and the corresponding range. It was found that practically linear relations existed, so that it was possible to set for any intermediate range desired by merely interpolating between the given settings. A split quartz prism was used.

PRELIMINARY STUDY.

A visual study of a great number of substances was made in order to find out what parts of the ultraviolet spectrum were most capable of exciting fluorescence, and also what substances respond best to such excitation, and were therefore suitable for further study. The Fuess spectrograph was mounted in such a way as to make the plane of the plate-holder horizontal. The substance was spread out on a piece of glass or stiff paper and held in the plane of the plate-holder. The following substances were examined in this way, a record being made in each case of the amount and position of the fluorescence excited by the ultraviolet *only* (since the dispersion in this region was good whereas the visible part was very narrow). The uranyl compounds exhibited the strongest fluorescence. They are given in the order of relative intensity, the first being the brightest.[1]

Rubidium uranyl nitrate,
Rubidium uranyl sulphate,
Potassium uranyl sulphate,
Potassium uranyl nitrate,
Potassium uranyl chloride,
Lead uranyl acetate,
Ammonium uranyl nitrate,
Mercury uranyl acetate,
Calcium uranyl acetate,
Strontium uranyl acetate,

[1] The following uranyl compounds were found to fluoresce most strongly under x-ray excitation: Rubidium uranyl nitrate, rubidium uranyl sulphate, cesium uranyl chloride and lithium uranyl acetate.

Ammonium potassium uranyl chloride, Uranyl acetate,
Cesium uranyl chloride, Sodium copper uranyl acetate,
Lithium uranyl acetate, Silver uranyl acetate,
Cadmium uranyl acetate, Uranyl tellurate,
Barium uranyl acetate, Thanous uranyl sulphate.

Other substances responding well to ultraviolet excitation were:

Anthracene, Phenolphthalein, } variable but continuous excitation between 550 and 200 mμ.

Calcium tungstate, Phosphorescent willemite, Fluorescein, Eosin, } excitation between 550 and 350 mμ and between 325 and 225 mμ approximately. Last two substances dissolved in water or alcohol.

The following substances fluoresced faintly by ultraviolet excitation:

CaC_2O_4, Cadmium phosphate,
Phosphorescent calcite.
Zinc silicate, Sodium uranyl cobalt acetate.
Zinc sulphate, Sodium molydate.

The following substances were practically unaffected by ultraviolet excitation:

Barium chloride,	Cesium chloride,	Sodium chloride,
Barium sulphate,	Didymium chloride,	Sodium silicate,
Berylium chloride,	Lead chloride,	Telluric acid,
Calcium fluospar,	Naphthol yellow,	Thallun sulphate,
Calcium sulphate,	Potassium iodide,	Tungstic acid,
Cadmium iodide,	Rubidium chloride,	Vanadium chloride,

and the oxides:

Al_2O_3,	CaO,	Cr_2O_3,	PbO,	NiO,	SiO,	UO_3,
BaO,	CeO_2,	CuO,	MgO,	Ni_2O_2,	SnO_2,	ZnO.
Bi_2O_3	CeO,	FeO,	MnO,	Sb_2O_3,	TeO_2,	

Three general types of excitation were observed. First, a broad continuous region of excitation, somewhat variable in intensity and becoming gradually weaker further out in the ultraviolet. Second, strong in the violet and near ultraviolet to about 350 mμ where the fluorescence seems to dissappear over about 25 mμ then to reappear over a region about 100 mμ long with a maximum at about 275 mμ. Third, strong in the violet and near ultraviolet to about 350 mμ where the intensity drops very rapidly to practically zero in some cases or to a relatively small value beyond which point the intensity gradually fades away. No fluorescence was observed beyond 200 mμ. Anthracene is a good example of the first type, calcium tungstate and fluorescein are good examples of the second type, and the uranyl compounds illustrate the third type.

Photographs were obtained of the fluorescent light emitted from nearly all of the substances listed above which show any appreciable effect. The means of mounting the material is described in the following paragraph. It was very difficult to secure good photographs in some cases, particularly with the liquid solutions of fluorescein and eosin. The Fuess spectrograph was used and a camera lens of 7 inches focal length. Exposures ranging from one minute to thirty minutes were necessary.

METHOD OF MOUNTING THE FLUORESCENT SUBSTANCE.

It was necessary to have the fluorescent material offer a smooth surface to the exciting light in order to obtain a good record on the photographic plate, to which end the following simple method was used. A strip of varnish or glue about two centimeters wide was made across the whole width of the plate, and the powdered substance was sprinkled over this with sufficient depth to cover it completely. Another glass plate was then used to press upon on rub this surface till it was made as smooth as possible. Care was taken not to leave any part of the surface in a matte white condition due to rubbing, as such a part may appear on the photograph to be different from its surroundings. In case of some of the uranyl salts the natural crystals are very hard to reduce to fine enough granulations to make a smooth surface possible in this way. Some of the photographs show this. In case of liquids or solutions a strip of quartz was used, and it was mounted in such a way as to cover the portion of liquid to be exposed.

FURTHER STUDY OF THE URANYL COMPOUNDS.

It was mentioned above that the uranyl compounds were excited to fluorescence by wave-lengths of light lying between 550 mμ and 350 mμ. (Excitation by shorter wave-lengths than this was very feeble, too faint indeed to be photographed.) In the most intense part of the excitation, as photographed by the Fuess spectrograph, there appears to be a short region in which the excitation is variable, giving what might be called bands, and this region is the same as that in which absorption bands for these same materials are found. Now fluorescence is undoubtedly due primarily to absorption, though it cannot be assumed that greater absorption will produce proportionately greater fluorescence. It seems reasonable nevertheless to expect that there may be some variation in the excitation where there is variable absorption. If it is true that the variation in the intensity of the fluorescence is due to the changing absorption of the dispersed exciting light, this method might well be used in detecting and studying the absorption of materials, for if light of a

particular wave-length is absorbed and this excites fluorescence which emanates from the same, or neighboring, spot, it would be very easy to observe this photographically in case there is good dispersion of the exciting light. The work that follows is an attempt first to test the validity of the assumption by seeing if fluorescence bands *do* occur where absorption bands are known to exist, and, if the results confirm the assumption, to locate the position of as many absorption bands as this method is capable of giving, and thereby to test the laws which have been found to govern the arrangement of the bands previously observed. The uranyl salts are particularly good for this work because they give many narrow bands, both in the fluorescence region of the spectrum and in the absorption region.

THE FOLLOWING ARE THE COMPOUNDS TESTED:

1. Barium uranyl acetate,
2. Lithium uranyl acetate,
3. Mercury uranyl acetate,
4. Strontium uranyl acetate,
5. Uranyl acetate,
6. Sodium copper uranyl acetate,
7. Cesium uranyl chloride,
8. Potassium uranyl chloride,
9. Potassium uranyl nitrate,
10. Rubidium uranyl nitrate,
11. Cesium uranyl sulphate,
12. Rubidium uranyl sulphate.

Nichols and Howes[1] in their recent treatise entitled "Fluorescence of the Uranyl Salts" give a summary of results showing the distribution and character of the fluorescence spectrum and the absorption spectrum of many uranyl compounds. It is shown that the spectrum of the fluorescent light consists of bands which naturally form eight groups of five members each, approximately, ranging from 640 mμ to 490 mμ, or thereabouts. The absorption spectrum consists also of bands having about the same arrangement, but ranging from 490 mμ to 380 mμ, apparently a continuation of the fluorescence spectrum. The frequency intervals (reciprocal wave-length intervals) between homologous bands of each group are practically the same throughout the spectrum of either, the interval being about 86 in the fluorescence spectrum and about 70 in the absorption spectrum. The last member of the fluorescence series is usually coincident with or at a distance from the first member of the absorption series of the homologous band of 86 or 70 frequency units. Considering all of the series of the various homologous bands there is an overlapping of the fluorescence and absorption spectra of about three groups, called the "reversing region" because here there are coincidences of fluorescence and absorption bands.

In this work a glass-bulb nitrogen-filled tungsten lamp, running at 6 amperes, was used as a source of ultraviolet light. A quartz mercury

[1] Nichols and Howes, Carnegie Inst. Wash. Pub., No. 298, 1919.

lamp was used[1] for calibration purposes, the calibration spectrum being photographed alongside of the other spectrum by exposing an adjacent portion of the slit of the spectrograph, both exposures taking place at the same time.

The intensity of blackening of the plates was measured by means of a device set up by J. O. Perrine in connection with his work[2] on "A Spectrographic Study of Ultraviolet Fluorescence Excited by X-rays." The apparatus makes use of a photo-electric cell, *C* in Fig. 2, and a sensitive galvanometer *G*. The cell, which was selected after trial of several types, was made by Kunz.[3] A Leeds and Northrup type *C* galvanometer was used about 6 meters from the scale near the comparator and cell. The comparator carried the photographic plate *P* just under a slit 2 mm. by .25 mm., through which a strong beam of light from an incandescent lamp *L* was passed. The lamp had one filament carrying a current of about 6 amperes from a storage battery. The current could be adjusted to meet the needs of the plate. *E* is a constant potential dry battery of about 80 volts. Further description of the apparatus is given in the paper just cited.

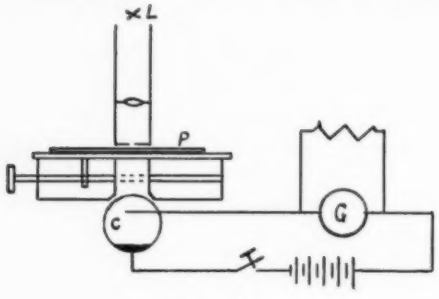

Fig. 2.

Much of the success of the present work is due to this apparatus. The instrument, which is highly sensitive to any variation in the density of the photographic image, has many advantages over other methods such as those depending on the eye, but faulty places in the photograph must be carefully avoided or eliminated by comparison with other photographs.

METHOD OF PLOTTING.

Curves were first made from the galvanometer deflections and the positions on the comparator. The intensities of the light transmitted by the negative were plotted as ordinates and the comparator readings as abscissæ, these plots being made while the measurements were being made, *i.e.*, plotting rather than recording the numbers. The intensities are merely relative, so that a convenient arbitrary scale was chosen to represent them. The positions of the mercury lines were located on the

[1] The well-known, yellowish green fluorescence of these substances is of a color to which most photographic plates do not respond well. The most satisfactory of the numerous plates tested was found to be the polychrome plate made by the Eastman Kodak Company.

[2] J. O. Perrine; Thesis in M.S. in Cornell University Library.

[3] Kunz and Stebbins, PHYSICAL REVIEW, 7, p. 282.

plot by observing the comparator reading for the smallest deflection of the galvanometer; thus the densest part of the line was taken as the proper position of the line. A setting could be made to the nearest tenth of a millimeter. Five to seven mercury lines were thus located on each plot. Knowing their wave-lengths to four significant figures their reciprocals were plotted (on another sheet) as ordinates against their recorded positions on the plot as abscissæ, and thus a calibration plot was obtained, giving the reciprocal wave-lengths for any comparator reading on the first plot. Using this calibration plot the final plot was obtained where the intensities of the light were plotted against the reciprocal wave-lengths. A new calibration plot was used whenever the mercury lines were found to be spaced differently due to different magnifications caused either by a change in the settings of the spectrograph or by a change in the camera adjustment. Final curves were made in this way for each of the twelve uranyl compounds.

In these plots a millimeter represents 2.5 frequency units,[1] and one tenth of a millimeter on the photographic plate. The accuracy of the data recorded in Tables I. to V. is such that the results are probably correct to within three frequency units. An estimated "probable error" is near one frequency unit. Typical curves are presented, greatly reduced, in Figs. 3, 4, 5 and 6.

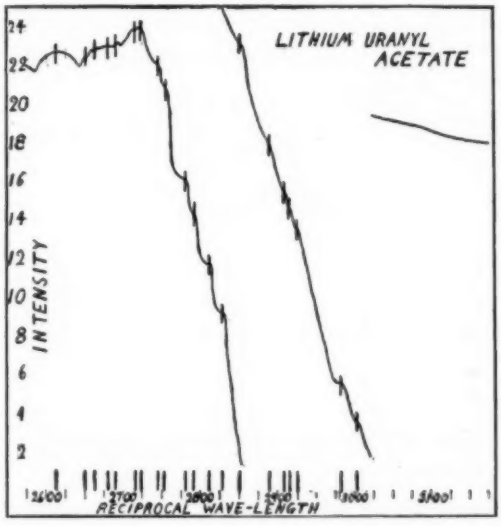

Fig. 3.

[1] A frequency unit is such that 500 mμ corresponds to 2000 frequency units, *i.e.*,

$$\frac{1}{.000000500 \text{ in meters}} = 2000 \times 10^3.$$

Peaks in the curves represent regions of greater fluorescence. They are undoubtedly regions of greater absorption, and many of them coincide with absorption bands of these substances that have been located by

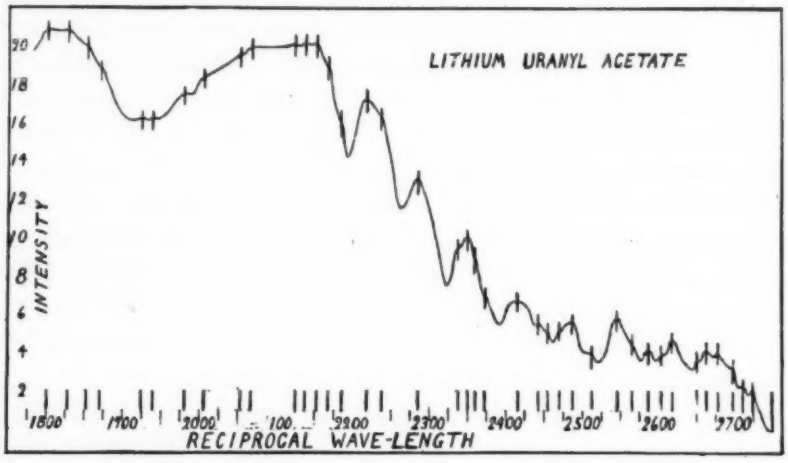

Fig. 4.

other methods. The data in the tables are arranged in two columns so as to show the agreement of the results obtained by this method and measurements made by other methods. The first column shows the

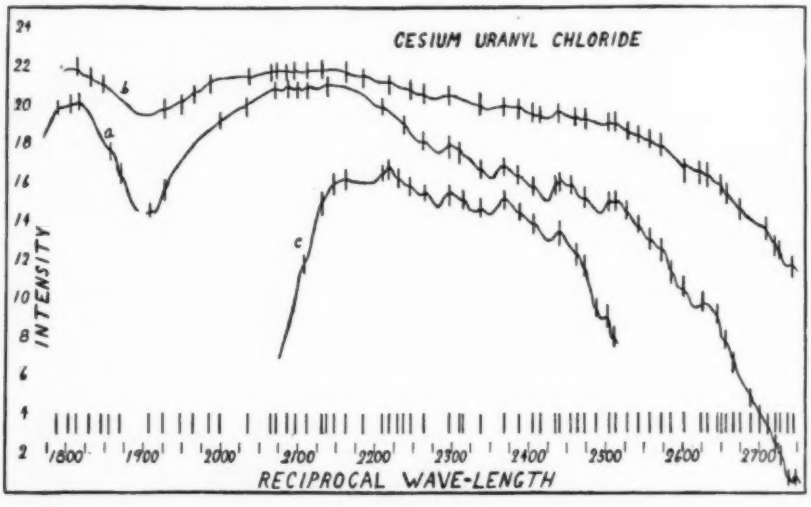

Fig. 5.

former, the second column the latter as published by Nichols and Howes. The photo-electric cell is so sensitive as to detect bands that are not apparent to the unaided eye. Data for these fainter bands seem to check

equally well, therefore credence is given to these also. Wherever there is a marked difference in the direction of the curve such as to indicate a partially resolved band and wherever the main part of an unresolved band appears there is a short vertical line drawn through the curve, and these lines appear again at the bottom of the plot. The bands have been designated by the same symbols used by Nichols and Howes. In cases where bands could not be identified, symbols were assigned so as to agree as nearly as possible with those of the same class, *e.g.*, the acetates, nitrates, etc., as determined by Nichols and Howes.

Extension of the Absorption Region.

Some of the photographs show very distinctly that the absorption bands extend further into the ultraviolet region than it has been possible

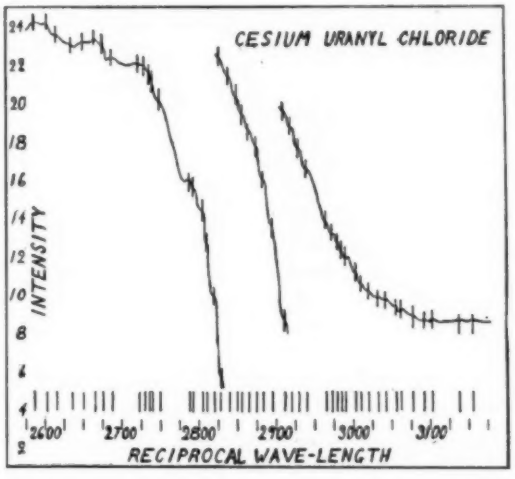

Fig. 6.

to go by the other methods. Cesium uranyl chloride is particularly rich in bands throughout the region covered by the photograph. It has been known that this substance is more fully resolved at ordinary temperatures than most of the other uranyl compounds. In order to see if the bands really extend as far as there is any fluorescence excited, a few long-time exposures were made, the range being 390 mμ to 310 mμ. A quartz-bulb nitrogen-filled tungsten lamp was used. An exposure of two hours was found to be sufficient to register all of the bands that could be recorded by the photographic plate. Further exposure only made the black part of the plate darker and made the detection of the bands by the photo-electric cell more difficult. In fact it was necessary to have regard to the time of exposure in all cases in order to obtain proper

TABLE I.

Bands Appearing in Two or More Curves for Cesium Uranyl Chloride.

Range 550 mμ to 370 mμ, approximately. See Fig. 5.

	Curve *a*, 1/λ.	Curve *b*, 1/λ.	Curve *c*, 1/λ.	Curve on Fig. 6.
B_1	1812	1810	....	
D	1925	1925	....	
E_2'	2032	2035	....	
d	2070	2072	....	
d′	2086	2085	....	
e_2'	2098	2095	....	
b	2113	2113	....	
b_3	....	2131	2130	
d	....	2148	2145	
d_2''	....	2162	2162	
d′	2210	....	2210	
d	....	2218	2218	
e_2''	....	2245	2245	
b_2'	2263	2263	2265	
d_2'	2298	2296	2297	
b_2	2337	2336	2337	
d_2	2367	2365	2368	
e_2''	2385	2388	2388	
b_2'	2405	2405	2405	
d_2	2440	2438	2440	
a_1'	....	2462	2464	
b_2'	2473	2475	2473	
d_2'	2505	2505	2503	
d_2	2512	2512	2510	
e_2''	2528	2530	....	
b_2'	2543	2543	....	
b_2	2557	2557	....	
d_1''	2572	2572	....	
d_2	2586	....	....	2586
e_2''	2600	2602	....	2602
c	....	2632	....	2633
d	....	2650	....	2650
e	2657	2657	....	....
a	....	2675	....	2675
b_2'	2687	....	....	2686
d_1''	2712	2710	....	....
d	2722	2722	....	2722
e	2730	2728	....	....

sensitiveness in measuring the plates. Too long exposures tend to fill up the places between the bands and destroy the contrast.

All of the twelve compounds were photographed for the range 390 mμ to 310 mμ, measurements were made, and the data plotted in the same manner as in the case of the first range. Since the first range extended

from about 550 mμ to 370 mμ, there was an overlapping of about 20 mμ. This repetition aided in establishing the reality of the bands. Only for cesium uranyl chloride were there independent measurements made with the photo-electric cell from different photographs over the first range. These are plotted on the same sheet (Fig. 5). There is also a curve to show the effect of placing a screen between the substance and the plate

TABLE II.

Barium Uranyl Acetate.		Lithium Uranyl Acetate.		Uranyl Acetate.	
B. Values of 1/λ.	N. & H. Values of 1/λ, p. 161, 167.	B. Values of 1/λ.	N. & H. Values of 1/λ, p. 158, 164.	B. Values of 1/λ.	N. & H. Values of 1/λ, p. 149.
1805 I		1800 A		1788 E_1	1791 E_1
1830 D	1828 D	1827 C	1825 C	1803 F	1802 F
1862 H		1852 F	1852 F	1820 G	1817 G
1888 I		1870		1860 B	1857 B
1925 E	1923 E	1924 D		1913 H	1912 H
1943 G	1942 G	1938 F	1936 F	1965 E	1965 E
1975 I		1980 I		1988 G	1989 G
2018 F	2017 F	2005 D	2005 D	2028 B	2029 B
2032 H		2052 h		2039 C′	2039 C′
2070 C		2068 h′		2053 F_1	2056 F_1
2085 D	2086 D	2125 h	2124 h	2075 G	2073 G
2100 F	2101 F	2138 h′		2088 H	
2125 G′		2152 c′		2100 e′	
2155 c		2168 c		2120 f′	
2210 g′		2185 e	2185 e	2150 d	
2245 e′		2219 c′		2173 e′	
2275 gh	2276 gh	2238 c	2235 c	2210 i	
2305 c″		2285 c		2215 g	
2345 gh		2338 h		2223 d	
2365		2350 h′		2260 f′	
2395 e	2394 e	2360 c′		2270 k	
2420 gh	2419 gh	2373 c	2373 c	2281 i	
2450 f′		2415 h′		2303 c	
2475 g		2443 c	2446 c	2315 e′	
2488 gh	2487 gh	2455 f		2323 e	
2502 c		2470 e		2340 k	
2520 f′		2488 h′		2353 d	
2530 e″		2513 c	2515 c	2388 f	
2548 g		2545 h		2412 k	
2560 gh		2565 c		2445 c	
2568 c′		2586 c	2585 c	2465 e	
2578 c		2603 g		2490 i	
2600 e″		2610 e		2503 d	
2615 g		2618 h		2518 c	
2626 h′		2635 c		2538 e	
2632 gh		2650 c		2547 f′	

TABLE II.—*continued.*

Barium Uranyl Acetate.		Lithium Uranyl Acetate.		Uranyl Acetate.	
B. Values of $1/\lambda$.	N. & H. Values of $1/\lambda$, p. 161, 167.	B. Values of $1/\lambda$.	N. & H. Values of $1/\lambda$, p. 158, 164.	B. Values of $1/\lambda$.	N. & H. Values of $1/\lambda$, p. 149.
2665 e′		2663 c		2557	
2688 g		2678 e		2563 i	
2707 c′		2688 h		2576 d	
2728 f′		2698 h′		2585 c	
2738 e′		2711 c′		2593 e′	
2748 e		2724 c		2602 f	
2757 g		2743 g		2607 e′	
2770 gh		2750 e		2618 f′	
2790 c″		2778 c		2633 i	
2805 e′		2790 c		2638 g	
2815 e		2810 g		2653 c	
2843 gh		2828 h		2675 e	
2855 c		2850 c′		2680 x	
2867 f′		2889 e		2690 f′	
2877 e′		2907 h′		2697 k	
2888 e		2915 c		2708 g	
2905 h′		2925 c		2718 d	
2922 c′		2982 c		2740 f	
2930 c″		3003		2748 x	
2943 e′				2763 k	
2978 gh				2777 g	
2995 c				2789 d	
3030 e				2813 e	
3085 e′				2825 f′	
3122 c′				2838 k	
3148 f′				2848 g	
				2880 e	
				2923 d	
				2948 e	
				2973 k	
				3028 x	
				3057 g	
				3075 d	
				3118 k	
				3128 g	
				3143 d	
				3165 x	

with the hope of screening off some of the visible light diffusely reflected from the substance. This procedure was however not satisfactory. One purpose of the three plots (or curves) for cesium uranyl chloride is to show how well the bands check. The data are given in Table I. Bands that appear in two or more curves are given in parallel columns. It can be seen that the differences are few in number and are well within the experimental error.

DISCUSSION OF RESULTS.

In Tables II. to V. comparison is made with former data obtained when the substance was at the temperature of liquid air, − 185° C. This seems justifiable because of the fact that some of the compounds are partially resolved at room temperature, so that the components, which are separated quite well by the relatively large dispersion of the spectrograph, show up well when measured by the photo-electric cell.

A comparison of the results obtained by the present method with those of other methods seems to establish the fact that *the position of the absorption bands can be determined by the fluorescence that the absorption gives rise to*, a fact already established by Howe[1] in the case of certain phosphorescent sulphides. Not all absorption bands may have the

TABLE III.

Potassium Uranyl Nitrate.		Potassium Uranyl Chloride.		Rubidium Uranyl Sulphate.	
B. Values of $1/\lambda$.	N. & H. Values of $1/\lambda$, p. 139.	B. Values of $1/\lambda$.	N. & H. Values of $1/\lambda$, p. 90–93.	B. Values of $1/\lambda$.	N. & H. Values of $1/\lambda$, p. 174, 178.
1795 D	1794 D	1761		1810 I	1812 I
1823 I	1824 I	1787 A_1	1785 A_1	1822 A′	
1860 B	1862 B	1815 C_1	1816 C_1	1842 C	1844 C
1978 E	1976 E	1945 E_2'	1940 E_2'	1872 F	1872 F
2005 J	2007 J	1987 C_2	1988 C_2	1907 A′	1908 A′
2070 F	2069 F	2012 d_3	2014 d_3	1948 E	1947 E
2093		2085 d_2		1957 F	1955 F
2127 d		2155 d_3	2155 d_3	1990 A′	1992 A′
2162 f		2237 e_2'		2012 C	2011 C
2188 l′		2268 c_2'	2264 c_2'	2063 b_1	2066 b_1
2268 d	2269 d	2335 c_2'	2333 c_2'	2078	
2337 d		2375 e_2'	2375 e_2'	2093 e_1	2096 e_1
2372 f	2369 f	2390 a	2392 a	2133 b_1	2137 b_1
2394 l′	2397 l′	2456 a_1	2456 a_1	2165 e_1	
2425 j		2468 c_2		2190 g	2188 g
2450 k		2477 c_2'		2205 b_1	2206 b_1
2492 j		2530 a_2''	2533 a_2''	2238 e_1	
2522 k		2548 c_2'		2268 h	2267 h
2535 l′		2595 a_1	2595 a_1	2282 c_1	
2563 j		2613 c_2'		2300 d	2301 d
2580 f		2626 d_1		2322 g_1	2322 g_1
2605 l′		2655 e_2'		2340 h	2341 h
2618 d		2665 a_1		2375 e_1	2375 e_1
2637 j		2675 c_2		2410 h	2409 h
2655 f		2698 d_1		2420 b_1	
2675 l′		2726 e_2'		2430 c	
2703 j		2737 a_1		2450 e_1	2450 e_1
2722 f		2755 c_2'		2482 h	
2745 l′		2782 d_3		2498 c_1	

[1] Trans. Am. Philos. Soc., LVI., p. 259 (1917).

TABLE III.—*continued.*

Potassium Uranyl Nitrate.		Potassium Uranyl Chloride.		Rubidium Uranyl Sulphate.	
B. Values of 1/λ.	N. & H. Values of 1/λ, p. 139.	B. Values of 1/λ.	N. & H. Values of 1/λ, p. 90–93.	B. Values of 1/λ.	N. & H. Values of 1/λ, p. 174, 178.
2757 d		2800 b_1'		2522 e_1	
2798 k		2807 a_1		2550 h	
2813 l′		2818 c_2		2572 c	
2853		2835 d_1		2585 d	
2883 l′		2850 d_3		2606 g_1	
2898 d		2876 a_1		2622 h	
2915 j		2887 c_2		2637 c_1	
2928 f		2898 c_2''		2653 d′	
2953 l′		2918 d_3		2667 e_1	
2983 j		2939 b_1'		2680 g	
3032 d		2950 c_2		2705 c_1	
3050 j		2968 c_2''		2715 c	
3075 k		2998 e_2'		2724 d	
3100 d		3018 a_1		2738 e_1	
		3042 d_1		2745 g_1	
		3080 b_1'		2757 h_1	
		3100 c_2'		2782 c_1	
		3128 d_3		2803	
		3151 a		2820 g	
				2838 b_1	
				2855 c	
				2898 h_1	
				2915 c_1	
				2930 c	
				2949	
				2978 b_1	
				3000 c	
				3040 h_1	

power of exciting fluorescence, and, if so, such bands would not appear on the plate. This may explain why some bands are missing by this method. Most of the known bands do appear however and many more besides. Where formerly the absorption spectrum was observed only between 490 mμ and 380 mμ, approximately, *the range is extended by this method in both directions, i.e.*, 550 mμ to 322 mμ, or through a frequency range of 1800 to 3100. In the extension toward the shorter wavelengths the bands readily fall into the series already determined, a fact which strengthens the belief that all regions showing fluorescence really serve to locate absorption bands.

In a few instances there seemed to be a new series starting somewhere near the middle of the complete absorption region, but more observations are needed to establish this if such is the case. Series of this sort are

indicated by letters in the latter part of the alphabet. Again, there is some indication that the intensity of the members of the series varies as we go through the spectrum, resulting in more than one maximum. If this is true it may explain the apparent omission of a part of the series due to the faintness of the bands, as can be noted in some cases.

Reversing Region.

The so-called reversing region lies within the seventh, eighth and ninth groups of the fluorescent spectra, *i.e.*, 2,000 to 2,200 frequency units

Table IV.

Cesium Uranyl Sulphate.		Strontium Uranyl Acetate.		Sodium Copper Uranyl Acetate.	Mercury Uranyl Acetate.	Rubidium Uranyl Nitrate.
B. Values of $1/\lambda$.	N. & H. Values of $1/\lambda$, p. 175, 178.	B. Values of $1/\lambda$.	N. & H. Values, p. 160, 166.			
1795 E	1794 E	1810		1820 C	1798 A	1788 D
1815 G	1813 G	2000 D	2004 D	1873 B	1812 B	1807 F
1845 B	1848 B	2050 H	2046 H	1975 A	1885 B	1840 K
1864 C	1861 C	2128 h′		2000 D	1980 C	1852 L
1903 G		2200 h′	2206 h′	2040 B	2015 c′	1910 I
1915 I	1913 I	2270 h	2274 h	2080 C	2030 c	1923 K
1952 D	1954 D	2287		2100 f	2085 c′	1960 D
1990 H	1993 H	2302 j		2128 b	2150 h	2045 D
2018 i		2337 h′		2152 h	2200 g	2095 K
2035 c′	2036 c′	2350 i	2350 i	2205 g	2218 h	2120 l′
2050 E	2052 E	2400 e″	2400 e″	2263 f_1	2252 e	2193 l′
2063 f	2061 f	2437 a		2275 g	2320 e	2218 δ
2080 h	2077 h	2516 j		2300 h	2365 c′	2270 d
2087 i	2085 i	2544 h′		2340 g	2405 h′	2295 h
2102 c	2104 c	2578 a		2365 h	2427 h	2338 d
2138 g		2613 h′		2410 g	2455 d	2360 δ
2147 g′	2144 g′	2655 j		2420 i	2493 i	2375 f
2165 a	2165 a	2680 e″		2473 f_1	2514 c	2390 l
2192 e		2695 h		2538 f_1′	2532 e	2402 l′
2222 g′		2718 a		2564 i	2563 i	2432 h
2232 a		2732 b		2573 h	2590 f	2473 l′
2280 g	2280 g	2770 i		2590 f	2602 e	2505 h
2290 g′		2799 b′		2605 f_1′	2622 g	2527 l
2307 a		2811 c		2620 g	2633 i	2550 d
2320 c′		2820 e″		2627 g′	2660 f	2570 δ
2352 g		2835 h		2632 i	2677 f_1	2585 f
2372 a		2875 b		2655 c′	2703 i	2595 l
2405 e		2903 h		2660 f	2707 h	2618 d
2428 g′	2427 g′	2928 a		2675 f_1′	2722 c	2626 e
2460 c′		2945 b		2680 f_1	2732 f	2635
2480 e′		2965 h′		2688 g	2738 d	2649 x
2500 g′	2498[1]	2975 h		2703 i	2755 h′	2655 f
2530 c′		3010 b′		2713 h	2770 c_1	2660 k

[1] No letters assigned.

TABLE IV.—*continued.*

Cesium Uranyl Sulphate.		Strontium Uranyl Acetate.		Sodium Copper Uranyl Acetate.	Mercury Uranyl Acetate.	Rubidium Uranyl Nitrate.
B. Values of $1/\lambda$.	N. & H. Values of $1/\lambda$, p. 175, 178.	B. Values of $1/\lambda$.	N. & H. Values, p. 160, 166.			
2543 e	2543[1]	3020 c		2728 f	2780 h	2670 l
2550 e′		3093 c		2753 f_1	2799 f	2680 l′
2568 g′	2567[1]			2770 i	2823 f_1	2698 e
2578 i				2780 h	2835 g	2712 h
2595 c				2793 c′	2850 h	2730 k
2605 d_1				2813 f_1′	2898 h′	2743
2615 e	2613[1]			2835 g′	2910 c_1	2750 l′
2626 f′				2850 h	2921 h	2755 d
2643 g′				2863 c′	2960 f_1	2770 e
2675 d_1				2876	2978 c_1	2780 S
2692 e′				2903 g′	3015 f	2802 k
2703 g				2922 h	3050 c_1	2822 l′
2726 a				2934 f	3170 f_1	2827 d
2756 e				2968 g		2835 e
2770 g				3005 f		2859 x
2789 i				3040 g′		2865 f
2820				3068 c′		2870 k
2850 g′				3097 f_1		2898 d
2874 c				3168 f_1		2925 h
2885 d_1						2939 k
2906 e′						2953
2920 g′						2965 d
2928 i						2988 S
2947 c						3002 x
2975 e′						3010 k
2993 g′						3028 l′
3001 i						3045 e
3026 d_1						3075 f
3052 g						3089 l
3068 i						3118 e
3133 g′						3139 x
3168 d_1						3150 k
						3173 l′

approximately. This region is extended further toward the long wave lengths if credence is given to the bands herein contained and if these bands are due to absorption, for, if any point on the plate containing the fluorescent material is being excited to fluorescence by the absorption of light of a particular wave-length, this absorption being due to the fluorescent material itself, there is evidently a reversal wherever the wave-length of the exciting light is equal to the wave-length of a band of the fluorescence spectrum. In the tables there are shown several bands agreeing well with the bands of the fluorescence spectra, *i.e.*, as well as

TABLE V.

Cesium Uranyl Chloride.

B. Values of $1/\lambda$.	N. & H. Values of $1/\lambda$, p. 90–93.	B. Values of $1/\lambda$ con.	N. & H. Values of $1/\lambda$.	B. Values of $1/\lambda$ con.
1785 E_2'		2405 b_2'	2405 b_2'	2788 d_2'
1812 B_1	1810 B_1	2409 b_2	2410 b_2	2793 d_2
1828 C	1828 C	2415 b_3	2416 b_3	2804 e_2'
1845 D_1	1843 D_1	2435 d_2'	2436 d_2'	2810 e_2''
1855 D_2'	1854 D_2'	2440 d_2	2441 d_2	2819 b
1868 E_2''	1866 E_2''	2455 e_2		2828 b_2'
1906 B_3		2462 a_1'		2839 b_3
1924 D	1924 D	2474 b_2'	2476 b_2'	2850 d
1950 E_2''	1950 E_2''	2489 c		2857 d_2'
1963 A_2	1964 A_2	2505 d_2'	2509 d_2'	2865 d_2
1985 B_2	1985 B_2	2512 d_2	2513 d_2	2874 e_2'
1998 C_1	1998 C_1	2528 e_2''	2530 e_2''	2884 e_2''
2032 E_2'	2030 E_2'	2543 b_2'		2895 b_2'
2065 c	2064 c	2557 b_3		2911 c
2070 d'	2071 d'	2572 d_1''		2920 d
2085 d_2'	2086 d_2'	2586 d_2	2585 d_2	2930 d_2'
2098 e_2'	2100 e_2'	2601 e_2''		2940 d_2''
2107 a		2615 b_2'		2966 b_2'
2113 b	2114 b	2625 b_3		2973 b_2
2131 b_3	2132 b_3	2632 c		2980 b_3
2137 c_1'	2135 c_1'	2645 d_2'		2984 c
2147 d	2146 d	2650 d_2		2990 d
2162 d_2''	2164 d_2''	2657 e		3003 d_2
2185 b	2184 b	2665 e_2''	2670 e_2''	3010 d_2''
2210 d'	2212 d'	2675 a	2674 a	3020 e_2''
2218 d		2680 b		3032 b
2230 d_2	2229 d_2	2687 b_2'		3043 b_2
2238 e_2'	2239 e_2'	2693 b_2		3055 c
2245 e_2''	2245 e_2''	2702 c		3062 d
2263 b_2'	2263 b_2'	2712 d		3077 d_2''
2297 d_2'	2296 d_2'	2722 d_2		3092 e_2''
2310 e	2310 e	2730 e		3102 b
2315 e_2	2314 e_2	2736 e_2'		3137 d_2'
2337 b_2		2740 e_2''		3155 e_2'
2368 d_2	2369 d_2	2748 a		
2388 e_2''	2389 e_2''	2750 b		

the precision of the work warrants. These therefore indicate more reversals than have been heretofore obtained, and that the number of reversals in any one series is not limited to one, but may be as great as two or three.

It is rather curious that most of the new reversals are on the long wave-length side of the "reversing region" as given by Nichols and

Howes. In the cases of potassium uranyl chloride and rubidium uranyl sulphate none of the reversals by this method has been observed by other methods. This is true with cesium uranyl chloride, excepting the series E_2''. The methods give results that agree in series F of cesium uranyl sulphate. It must be admitted however that more data are needed in order to confirm or disprove the existence of the new reverasls. In cases where several photographs were made for the same substance there is a close agreement between the independent measurements, so that one is convinced that the method is capable of giving results quite comparable with those obtained by other methods.

The following table (VI.) shows the reversals of the bands in the various substances studied. The wave numbers in the first column are from Tables II. to V., and those to the right are from the tables given by Nichols and Howes on the pages indicated. Values in parentheses indicate that the corresponding band of the fluorescence spectrum is missing, or that it is not recorded by them. References are also missing for mercury uranyl acetate, sodium copper uranyl acetate, and rubidium uranyl nitrate, and they are therefore not included in the table.

TABLE VI.

Reversals of the Uranyl Bands.

Reversals by Present Method.	Reversals Observed by Nichols and Howes.
Barium uranyl acetate	(Pages 161, 167)
Series	
D reverses at 1830 and 2085	E reverses at 2009
F " " 2018 " 2100	
Potassium uranyl chloride	(Pages 88–101)
Series	
E " " 1925	
G " " 1943	
(H) " " (1862) " (2032)	
(I) " " (1805) " (1888) and (1975).	
Lithium uranyl acetate	(Pages 158, 164)
F reverses at 1852 and 1938	F′ at 2105 reverses approximately with f′ at 2109.
C " " 1827	
D " " 2005 " (1924)	
Strontium uranyl acetate	(Pages 160, 166)
D reverses at 2000	
H " " 2050	
Uranyl acetate	(Page 149)
E reverses at 1788	
F′ " " 1803	
G " " 1820, 1988 and 2075	
H " " 1913 (2088)	
B " " 1860, 2028	
E " " 1965	
C′ " " 2039	
F′ " " 2053	

TABLE VI.—*continued.*

	Cesium uranyl chloride	(Pages 88–101)
E_2''	reverses at (1785), 1868, 1950, 2032	B reverses at 1974
B	" " 1812	C " " 1993
C′	" " 1828	D " " 2005
D′	" " 1845	E " " 2026
D_2'	" " 1855	A " " 2037
D	" " 1924	E_2' " " 2030
A_2	" " 1963	E_2'' " " 2034
B_2	" " 1985	
C_1	" " 1998	
A_1	reverses at 1787	B reverses at 1969
C_1	" " 1815	C " " 1984
E_2'	" " 1943	D " " 2004
C_2	" " 1987	E " " 2022
		A_2 " " 2039
	Potassium uranyl nitrate	(Page 139)
D	reverses at 1794	
I	" " 1824	
B	" " 1862	
E	" " 1976	
J	" " 2007	
F	" " 2069	
	Cesium uranyl sulphate	(Pages 173, 178)
E	reverses at 1795	F reverses at 2061
G	" " 1815, (1903)	
B	" " 1845	
C	" " 1864	
I	" " 1915	
D	" " 1952	
H	" " 1990	
F	" " 2063	
	Rubidium uranyl sulphate	(Pages 174, 178)
I	reverses at 1810	E_1 reverses at 2028
A′	" " (1822), 1907, 1990	F " " 2038
C	" " 1842, 2012	G_1 " " 2045
F	" " 1872, 1957	
E	" " 1948	G " " 2049

SUMMARY.

Fluorescence is excited by wave-lengths of light between 550 mμ and 200 mμ, approximately. The intensity and range of excitation depends upon the substance.

There are three types of excitation observed:

1. Continuous, but variable in intensity, between 550 and 200 mμ.
2. Continuous, but variable in intensity, between 550 and 350 mμ.
3. Discontinuous, exhibiting a gap between 350 and 325 mμ, otherwise like type 1.

The range of the absorption spectra of twelve uranyl salts is extended to 550 mμ and to 320 mμ by the method herein discussed, a method

which makes use of the fluorescence excited by dispersed ultraviolet light, observing that wherever greater absorption takes place greater fluorescence results therefrom.

It is desirable to continue the work on the uranyl salts by this method, especially in the reversing region, because it is here that information can doubtless be obtained about the real mechanism of fluorescence.

The gap at 350 to 325 $m\mu$ in case of a few substances noted is rather curious. No explanation is given, but further study of this type of excitation is desirable. It was observed that one of the uranyl compounds, namely sodium uranyl cobalt acetate, appeared to the eye to give this type of excitation, but it was not studied photographically because of the relatively weak fluorescence produced.

The writer wishes to express his gratitude to Professor Ernest Merritt under whose guidance this work has been performed.

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SPECTRA OF HYDROGEN, NITROGEN AND OXYGEN IN THE EXTREME ULTRAVIOLET.

BY J. J. HOPFIELD.

SYNOPSIS.

Spectroscopy of Extreme Ultraviolet.—A method which has been developed of coating *films* with an emulsion suitable for work in this region is described in detail, and also an *oil-cooled discharge tube* of the internal capillary type which will stand an input of 2.25 KW and thus reduce the time of exposure and consequent fogging of the films from 10 to 100 fold. *Transparency of oxygen, nitrogen and air between 500* and *1,800* Å. was investigated. In a vacuum spectrograph with a grating of 50 cm. radius these gases were found to transmit light of from 1100 to 1225 Å. even when at a pressure of 3 cm. At around 1 mm. spectrum lines were photographed from 800 to 1,800 Å. and with oxygen at 0.001 mm., the spectrum was photographed to 430 Å. These gases, then, are not as opaque to light in this region of the spectrum as has been generally supposed.

Spectrum of discharge through hydrogen, 1,220 to 885 Å. The ultraviolet limit is the same for both continuous and disruptive discharges. Four spectrograms are reproduced and the wave-lengths are given for 90 lines below 1,059 Å., presumably due to hydrogen, as a continuous stream of pure gas was supplied. The resonance line was found superimposed in the fourth order on the $H\beta$ line; hence its wave-length is 1,215.68 ± 0.03 Å. This coincidence confirms the Bohr formula for this line, which is the first of the Lyman series.

Spectrum of Discharge through Nitrogen, 1,750 to 835 Å.—The continuous discharge gives chiefly the band spectrum of nitrogen, which is extended to 1,026 Å., the wave-lengths of 19 bands below 1,385 Å. being given. The wave-lengths of 50 new lines obtained with the disruptive discharge are also given and four spectrograms are reproduced.

Spectrum of Discharge through Oxygen, 1,863 to 507 Å.—Wave-lengths of about 100 new lines obtained with a disruptive discharge are given and six spectrograms are reproduced. *When mercury vapor was present* about 15 additional lines extending to 433 Å. were obtained.

Explanation of fluorescence observed around aluminum spark in air by Lenard in 1910, to a distance of 4 cm., may depend on the transparency of air to light of wave-length 1,000 to 1,400 Å.

INTRODUCTION.

IT has long been assumed by investigators in the extreme ultraviolet, that most gases, and especially oxygen are opaque in this region. As a consequence it was believed that it was practically impossible to study the ultraviolet spectrum of oxygen under the conditions which usually exist in a vacuum grating spectrograph. About a year ago, the author, supposing oxygen to be opaque, attempted to get its spectrum by using two gases, the one hydrogen and the other oxygen. These gases were kept localized, the opaque one filling only the discharge tube, and

the transparent one, hydrogen, the receiver. This was accomplished by suitably directing the two currents of gas.[1] The method was successful and suggested that after all oxygen might be transparent in the extreme ultraviolet. Following up this experiment was another in which both receiver and discharge tube were filled with oxygen, and in this case an extensive spectrum was obtained.[2] The spectrum of air also was obtained. This of course was expected in view of the transparency of nitrogen to 975 as found by Lyman,[3] and the now-established fact of the transparency of oxygen in this region.

There seems to be no especial difficulty, once the ultraviolet technique is acquired, in getting the spectrum of oxygen, and thus showing its transparency by obtaining its spectrum in the ordinary manner. In the progress of this research equipment was developed which when applied to the spectra of hydrogen and nitrogen yielded results that extended the spectra of these two gases. Other points of significance regarding these spectra were also brought out, hence these spectra as well as those obtained with oxygen will be described in this paper.

APPARATUS.

Most of the apparatus used was that ordinarily employed by investigators in this region of short wave-lengths, that is: a vacuum grating spectrograph, the necessary vacuum pumps, mercury traps, pressure gauges, generators for the gases used, driers, etc. The spectrograph, designed by E. P. Lewis and built in the department shop, consists of a sector-shaped cast brass box and holds at the smaller end, a concave grating of 50 cm. radius of curvature. This grating is of exceptionally fine quality. Within the larger end is a film-holder carried on a movable stage. This stage may be raised or lowered by rotation of a screw through a ground-glass joint, so that several exposures may be taken on the same film. This large end is also fitted with a broad flange against which the heavy glass lid is pressed. The plates were examined and measured on a Gaertner 20 cm. comparator. This comparator is the property of the Rumford Committee of the American Academy of Sciences, and was kindly loaned to the author by R. T. Birge for whose use the instrument was built. Furthermore, in order to fulfill the particular requirements of the research it became necessary to develop a special film for obtaining the photographs, and also a special discharge tube as the source of light. Since these last-mentioned articles of equip-

[1] PHYSICAL REVIEW, **18**, 327, 1921.

[2] SCIENCE, **54**, 553, 1921.

[3] Astrophysical Journal, 43, 89, 1916.

ment may be found useful to other investigators, they are fully described in the next few paragraphs.

Films.—The plates developed by Schumann could not be used to the best advantage on account of the large curvature of the focal field employed. Hence to obtain the spectrum in many orders in sharp focus, films sensitive to the ultraviolet were made. The method of making them is as follows:

Unexposed commercial films of the desired width are soaked in a solution of sodium thiosulfate until the emulsion is just dissolved. These films are then washed for three or four hours in running tap water, rinsed in distilled water and then dried.

Individual trays for the films are prepared as follows: Pieces of thin glass are cut one centimeter narrower and one centimeter shorter than the films to be prepared. (Old photographic plates from which the gelatine had been removed were used.) These glass strips, when fitted with two glass cross-pieces each, constitute the trays. These cross-pieces or feet, in order to hold the trays level on a levelled surface, are most conveniently made by drawing off pieces of *round* glass tubing, and labelling each pair of adjacent pieces with the same number by means of a file. The glass plate is then slightly warmed and a pair of these feet is stuck to it with warm red wax, care being taken to press them in contact with the plates. The spacing of the feet may be such as to divide the glass plate into segments of about the following ratios, 1 : 2 : 1. The diameter of the tubing employed may be any convenient one; about 5 millimeter for a 4 × 15 cm. plate is found satisfactory. To avoid disturbances due to surface tension, the shoulders of these short rods should not extend as far out as the edge of the trays. Mats of filter paper are cut to the size of the trays.

The trays with their mats (as many trays as films) are then mounted on a levelled table of glass. A good piece of window glass serves very well for this purpose if the films are not too large, otherwise plate glass is recommended. The mats, now on the trays, are each wetted with distilled water, about 10 c.c. being used for each 4 x 15 cm. mat. The films of the desired size are wetted in distilled water and placed upon the mats with the former emulsion side downwards. The following operations must now be carried out in a photographic dark room in brown light. The emulsion (a note on its preparation is given in a succeeding paragraph) about 20 c.c. per 5 x 16 film, is poured from a pipette over the film. If the emulsion does not immediately cover the film, it may be spread evenly by means of the pipette stem, and a little more added to replace any emulsion lost in the operation. The emulsion is then

allowed to settle for three or four hours after which time it is carefully drained off, the films stripped from the paper and hung up to dry.

For assistance in draining, a rail of small glass tubing is waxed to the left-hand edge of the glass table, and a small glass rod, "L"-shaped, is used to catch the feet of the trays in order to pull them around to this tripping rail. These feet also serve as handles while removing the films. To pin up the films for draining and drying, it is convenient to have a horn-tipped tweezers with a longitudinal groove cut on the outside of one of the tips and this channel to end in a transverse notch across both tips, so that the groove is towards the operator and the notch uppermost when the film is held by the tweezers in the right hand. Then pinning, even in the dark, is a simple matter, and there is little danger of either dropping or marring the film in the process. It is detrimental to the film to grasp it with the tweezers too soon after beginning to drain for the reason that the undrained liquid forms a surface skin over the emulsion; a slight contamination from the tweezers ruptures this skin and as a result a streak may extend the entire length of the film. To avoid this and at the same time save a minute in this preliminary draining, one may have three or four trays at the tripping rail inclined on corks, and they then will be well drained when needed. When the films are thoroughly dried, they are warped with emulsion side inward and then placed on edge in boxes for storage. The sides of these boxes should have been fitted with corrugated filter paper so as to hold the films separated and in place. In this manner a number of films may be packed into each box. These smaller boxes may be put into a larger one and thus the films, now provided with twofold cover, are well shielded from light.

The advantage of having warped films is evident when one is using them, for if by accident one is dropped onto the floor it always alights on its back; other advantages are easy storage, ready adaptability for mounting, for measurement, or for reproduction.

The method described above is readily adaptable, with only slight modification, to making plates. Evidently the process is not one of delicate technique, for if one plate or film is spilled the rest are unharmed, and even it is not spoiled for the wet mat keeps its bottom dry of emulsion.

One may use any ordinary commercial developer if diluted three- or fourfold with cold tap water. It may be used at room temperature. Fresh films are not sensitive; they become so in about a week, and then seem to increase in sensitiveness with age.

In the preparation of emulsion, the method devised by Schumann[1] was employed with a few modifications, namely; a good quality of French

[1] Baly, "Spectroscopy," p. 375.

pastry gelatine was used instead of Nelson's number one as recommended by Schumann, and only 50 to 60 per cent. as much as used by him, and the sensitizing temperature was varied between 60 and 40° C.

The films thus made proved very satisfactory in getting the spectrum of oxygen. They were less satisfactory for the spectrum of air, and failed almost completely on account of fogging when a long exposure was used in an attempt to extend the spectrum of nitrogen. It soon became evident that in order to get the spectrum of any gas that easily ionizes or forms corrosive compounds that attack the film, a short exposure, much less than an hour would be necessary. At a given pressure, the amount of fogging seems to increase rapidly with the time of exposure whatever the strength of the current might be. (It may be stated that my observations confirm those of Lyman, in that there seems to be for minimum fogging a certain nice balance between the current density, the capacity and induction in the circuit, and it may be added the heat produced in the discharge tube. With such adjustment an exposure of two hours in oxygen at 0.04 mm. pressure gave no appreciable fog on the film.) Hence a more intense source of light was needed, and a continuous input of more than 200 watts would soon destroy an ordinary tube of the internal capillary type. Thus to meet the need of this greater power capacity for producing a more intense light, an oil-cooled tube such as shown in the figure was designed and used.

Discharge Tube.—Description of the figure. *A* opens into the receiver of the vacuum grating spectrograph, *B* is an outlet to the pumps, the kerosene oil used for cooling is pumped in at *C* and leaves at *D*, *E* repre-

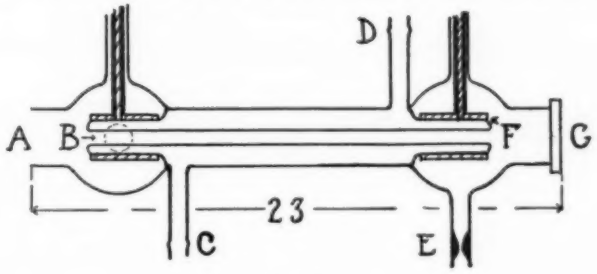

Fig. 1.

sents an inlet for gases if one wishes to use it. The capillary constriction is a safeguard against any of the drying chemicals being forced into the discharge tube by any sudden rush of gas. *F* is a cylindrical electrode in contact with the glass and is thus cooled by it. A quartz window is at *G*. This is used for getting the quartz-mercury-arc comparison spec trum. The tube is made of pyrex, has a total length of 23 centimeters,

and is represented approximately to scale. This tube was found to have a power capacity of about 2.25 kw. It reduced the time of exposure from one or two hours to as many minutes and hence satisfactorily solved the problem of fogging.

METHOD.

The film is placed in the receiver. A piece of heavy plate glass with a border of especially prepared rubber grease is pressed over the opening and the oil pump started. After a half hour the pressure in the receiver is reduced to 0.04 or 0.05 mm. The receiver is then rinsed with a small quantity of the dried gas to be studied, and 4 or 5 cm. of the gas admitted and allowed to stand for an hour in order to "season" the film, for this shrinks somewhat on being exposed to the dry atmosphere of the receiver. The gas is then pumped out, and, while the spectrum is being photographed, a steady stream of gas is kept flowing through the receiver into the discharge tube, leaving via B to the pumps. Since the average exposure is but two or three minutes per spectrum, this may easily be done without using a prohibitive quantity of gas. By properly adjusting the intake and rate of pumping the pressure in the receiver may be kept at any desired steady value and at the same time a fast circulation maintained. When low working pressures are desired in the receiver, a mercury condensation pump is used, and a mercury trap cooled with liquid air keeps the mercury vapor out of the receiver. It is also necessary when working at low pressures to admit the gases through long capillary tubes.

DESCRIPTION OF PLATES.

All the photographs described below are reproduced in Plates I. and II., but necessarily many details are lost in the reproduction. It is hoped, however, that most of the essential features will be evident.

Plate I., Figures 1 and 2.—Hydrogen, direct current 320 milliamperes, 3 mm. pressure, circulation, 2 minutes' exposure. This film shows some of the series lines of hydrogen. The resonance line is shown in four orders. It is evident that a large current density brings out the series lines in the ultraviolet. This resonance line is shown self-reversed in the three higher orders, and in the fourth order the self-reversed portion coincides exactly with the sharp line H_β of the Balmer series. H_γ and H_δ also appear on the prints. This coincidence of the resonance line with H_β at once furnishes not only an accurate determination of the wave-length of the former, namely, one fourth of that of H_β, but also checks its value as derived on the Bohr theory. The first statement is strictly valid because the spectra are obtained under practically vacuum conditions, hence the wave-lengths as found by coincidence of orders need not

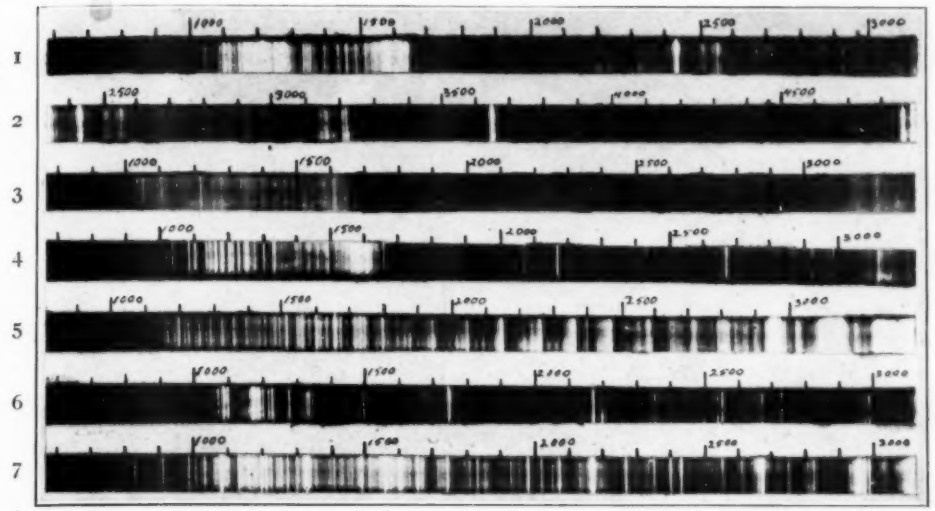

PLATE I.

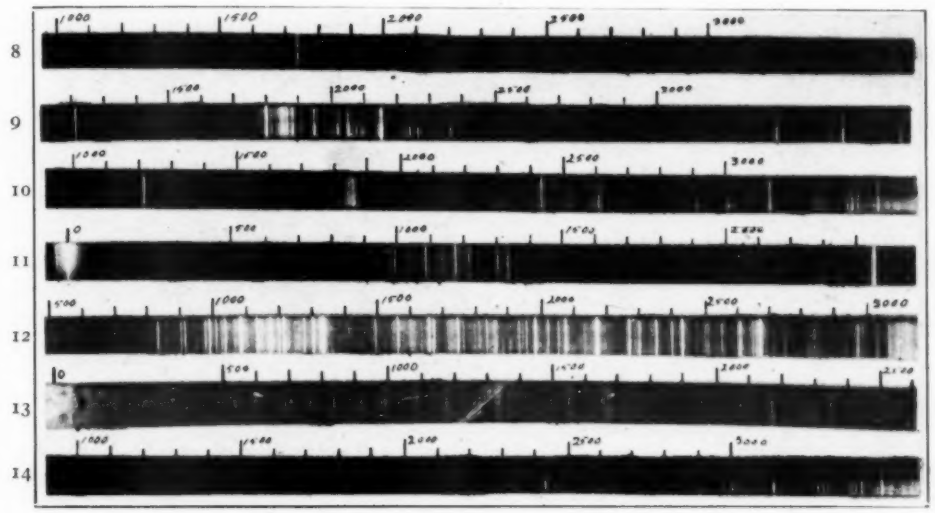

PLATE II.

J. J. HOPFIELD.

be modified for the varying dispersion of the medium. The accuracy of the application of the Bohr theory to this resonance line may be seen by comparing the formula for its frequency with that giving the frequency number of H_β. The first is given by

$$\nu_1 = R\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

and the last by

$$\nu_2 = R\left(\frac{1}{2^2} - \frac{1}{4^2}\right).$$

Hence one fourth the frequency number of the first is exactly the frequency number of the second. Thus the coincidence of the first order of the one line with the fourth order of the resonance line, as the theory would predict, has been found.

The wave-length of H_β as found by Curtis[1] and reduced to vacuum is 4862.677 Å. on the International System. Hence the wave-length of the resonance line is 1215.68Å. Owing to the unusually favorable conditions of observation, that is, a sharp line occurring in the middle of the reversed portion of a more diffuse line, it is thought that the probable error in this determination is about 0.02 or 0.03 Å. This indicates that the value attributed to this line by Lyman is too high by 0.3 Å., and that the value used by Millikan is more nearly correct. It is safe to assume, in the opinion of the author, that the best values of the other lines of the Lyman series are likewise the theoretical ones. Thus the first three that have been found by Lyman and which also occur on our plates (see Plate II., 12; Table VI.) have the following wave-lengths 1215.68, 1025.73, and 972.54 Å. These lines, which are readily obtained, may be used as standards in the ultraviolet where up to the present none have been established with an accuracy exceeding 0.1 Å.

Figure 3.—Hydrogen, direct current, 320 milliamperes, circulation, 8 minutes' exposure. This shows the extension of the secondary spectrum of hydrogen to 885.6 Å. The wave-lengths are recorded in Table I. Some of the lines recorded by Lyman[2] are also shown for the sake of comparison. (The wave-lengths in this table and subsequent ones were not measured in the expectation of great accuracy. It is hoped, however, that the individual values will be found accurate to at least 1 Å.) The continuous spectrum of hydrogen mentioned by Lewis[3] is shown on this plate in the region between 1680 and 1950 Å.

[1] Proceedings of the Royal Society of London, A 90, 605, 1914.

[2] "Spectroscopy of the Extreme Ultra-violet," p. 112.

[3] Science, 51, 947, 1915; PHYSICAL REVIEW, 16, 376, 1920.

TABLE I.

Hydrogen.

λ.	I.	λ.	I.	λ.	I.
885.6	1	955.3	4	1006.1	3
889.2	1	956.1	1	1006.4	4
892.5	1	957.7	2	1007.9	4
895.3	1	959.4	1	1009.6	2
903.1	1	960.5	2	1011.0	3
905.3	1	962.5	1	1012.4	4
906.7	1	963.5	3	1013.4	1
908.9	1	964.8	1	1014.6	1
911.5	2	968.9	1	1016.2	5
912.7	1	969.8	2	1017.3	4
916.9	3	970.9	4	1018.6	4
917.8	2	971.8	1	1021.3	3
919.9	4	975.4	1	1023.9	4
921.1	1	977.2	8	1025.8	8
922.4	2	978.8	8	1027.3	3
924.3	3	981.9	5	1029.4	2
927.4	2	984.4	1	1031.0	7
928.8	2	985.2	2	1034.6	7
929.5	2	989.0	3	1035.5	1
932.0	2	989.9	2	1036.9	4
935.6	5	991.1	3	1040.4	7
941.9	1	992.0	3	1044.7	4
942.6	1	993.8	1	1045.5	5
944.3	1	995.9	2	1047.1	7
946.2	3	997.1	2	1048.0	7
949.8	2	998.4	1	1049.2	4
950.6	2	999.4	1	1051.2	5
951.9	4	1001.4	4	1053.1	6
952.9	2	1002.3	4	1056.1	6
954.4	4	1004.4	3	1059.2	4

Figure 4.—Hydrogen, disruptive discharge, 0.02 mm. pressure, circulation, 20 minutes' exposure, mercury arc spectrum superimposed. No extension of the ultraviolet spectrum is observed under these conditions. The lines at λ 835, and λ 900 and many of the strong lines that appear throughout the entire spectrum are due to air.

Figure 5.—Nitrogen, direct current 324 milliamperes, 3 mm. pressure, circulation, 2 minutes' exposure. Table II. This spectrum is found to be principally a band spectrum extending to λ 1025.8, but many

TABLE II.

Nitrogen, Direct Current.

Line Spectra with D.C.		Lyman, λ.	Bands Degrading towards Red, λ.	Bands Degrading towards the Violet, λ.
λ.	I.			
1329.5	3		1054.5	1025.8
1412.4	3		1164.3	1033.3
1493.2	6	1492.8	1183.6	1046.7
1494.7	5	1494.8	1194.3	1067.0
1561.1	6		1213.9	1072.7
1657.2	6		1244.2	1086.0
1742.9	6	1742.7	1256.0	1110.4
1745.3	5	1745.3	1288.7	1152.2
			1322.7	
			1353.7	
			1384.7	

lines also occur. Lyman had previously explored the band spectrum of this gas to 1385 Å. The following evidence is offered showing that this new spectrum is probably due to nitrogen: It does not occur in either hydrogen or oxygen under the same or under any other conditions, when presumably the same impurities are present in these gases as in nitrogen. Of the line spectrum, two pairs shown in this table were found by Lyman[1] and the pair at λ 1493 was attributed to nitrogen, while the second pair at λ 1743 he states with less assurance is probably due to the same gas. The reason for this lack of certainty on his part as to the source of the above pair seems to be the possible impurities that might have been torn from the tube by the disruptive discharge used by him. That this pair is of the same origin as the first pair is indicated in the present experiment by the fact that it is produced by direct current in nitrogen, whereas the metallic lines of the electrodes which always occur when a disruptive discharge is used, never occur in this milder form of excitation. The other lines shown in Table II. are also probably due to nitrogen.

That a high-current density, such as used here, brings out line spectra not shown when smaller currents are used, is evidently due not only to the greater degree of ionization which must necessarily exist in order to carry the greater current, but also to the greater degree of molecular dissociation present at the high temperature that exists in the tube.

The near ultraviolet and visible spectrum as far as the green shown on our plates has not yet been examined for new lines.

Figure 6.—Nitrogen disruptive discharge, 1.5 mm. pressure, circulation, 2 minutes' exposure. Table III. This spectrum is of interest in that

[1] "Spectroscopy . . .," p. 113.

it shows that the transparency of the gas at this pressure exists to about λ 800. In parallel columns in the above table of wave-lengths are shown lines obtained by Lyman[1] in helium. In fact this table and subsequent ones contain all the lines, except two faint ones, obtained by him in helium. That his lines are due to air entering his spectrograph as an impurity, despite his great care in eliminating such impurities, rather than to helium, seems quite probable.

Figure 7.—Nitrogen, disruptive discharge, 0.02 mm. pressure, circulation, 20 minutes' exposure. The lines found by Millikan[2] on the refrangible side of λ 700 and ascribed to this gas were not found, perhaps owing to the opacity of the gas, which seems even more opaque than oxygen in this region.

Plate II., Figure 8.—Nitrogen, disruptive discharge, 3.5 cm. pressure, no circulation, 2 minutes' exposure. This film was taken in order to test the transparency of nitrogen. It was fogged because of the active nitrogen formed in the discharge tube and which spread into the receiver.

TABLE III.

Nitrogen—Disruptive Discharge.

λ.	I.	Lyman, Helium, λ.	λ.	I.	Lyman, λ.
834.9	2	834.8	1328.0	1	
838.3	1		1329.7	1	
917.2	2	916.7	1331.0	2	
978.1	3	977.6	1335.3	15D	
990.8	2	990.2	1343.7	4	
992.3	4	992.0	1345.5	3	
1006.8	1		1346.6	3	
1011.0	2	1010.6	1361.0	1	
1026.4	2	1026.0	1378.1	1	
1037.7	4	1037.0	1379.3	1	1379.5 Al.
1085.5	40	1084.9	1412.3	4	
1093.8	1	1086.1	1463.6	1	
1097.9	3		1467.6	1	
1101.3	4		1493.1	8	
1135.3	4	1134.7	1494.9	7	
1144.1	2		1536.2	1	
1152.7	1		1548.2	1	
1164.8	3		1551.0	1	
1168.4	4 Doublet		1561.2	8	
			1573.3	1	

[1] Astrophysical Journal, 43, 89, 1916.

[2] Proceedings of the National Academy of Sciences, 7, 289, 1921.

TABLE III.—*continued.*

λ.	I.	Lyman, Helium, λ.	λ.	I.	Lyman, λ.
1176.0	20 Complex	1175.5	1574.4	1	
1184.1	20 "	1176.3	1590.1	2	
1189.5	2		1593.2	2	
1191.3	1		1611.6	1	1611.8 Al.
1200.4	15	1199.8	1616.1	1	
1215.7	15	1216.0	1627.5	2	
1225.5	8		1629.1	2	
1229.0	6		1647.5	3	
1243.5	4		1650.0	4	
1247.8	3	1247.9	1657.2	8	
1258.9	1		1670.5	1	
1261.7	1		1675.8	6	
1270.3	2		1677.8	2	
1276.0	10				
1280.6	1		1703.5	1	
1300.6	1		1718.5	1	1718.3 Al.
1311.0	5		1740.2	5	
1319.6	5		1742.7	10	
1324.2	4		1744.9	8	
1326.9	1		1747.5	4	
			1751.3	6	

From considerations of the dimensions of the spectrograph used, and the pressure of the gas as stated above, it is evident that a layer of nitrogen 4.5 cm. thick and at atmospheric pressure is easily transparent down to 1070 Å. More will be said concerning this in a subsequent paragraph.

Figure 9.—Oxygen, direct current 320 milliamperes, circulation, 3 mm. pressure, 14 minutes' exposure. This plate shows clearly the absorption band of oxygen first observed by Schumann. In the neighborhood of λ 1300 is shown the transparent region whose less refrangible edge was located by Lyman[1] and whose more refrangible edge was found by the author at about λ 1000. The short wave-lengths shown in the plate are λ 1215.7, λ 1217.7, λ 1302.5, λ 1305.2, and λ 1306.4. The first is the resonance line of hydrogen and the others are probably oxygen lines. The last three lines might easily be mistaken for a triplet, except for the fact that their relative intensities vary with the nature of the discharge used. Thus with a disruptive discharge λ 1302.5 is strongest, while with direct current such as used here it is weakest. The last two probably

[1] "Spectroscopy of the Extreme Ultra-violet," p. 64.

form a doublet. The bands near λ 1800 are presumably CO and O_2 bands.

Figure 10.—Oxygen, disruptive discharge, 1.5 mm. pressure, circulation, 2 minutes' exposure. Table IV. Besides the lines on the more

TABLE IV.

Oxygen Disruptive Discharge.

λ.	I.	λ.	I.
1036.8	5	1743.1	5
1083.7	4	1745.7	4
1109.7	4	1752.3	3
1128.4	8	1760.9	8
1129.4	5	1781.4	7
1130.3	4	1787.0	7
1132.3	10	1799.7	4
1142.1	5	1821.9	3
1143.8	7	1854.7	6 Al.
1147.5	7	1862.8	8 Al.
1149.2	3		
1158.7	5		
1167.7	7		
1168.5	5		
1189.7	5		
1215.7	15		
1217.8	10		
1277.7	8		
1302.5	10		
1305.2	8		
1306.4	7		

refrangible side of the absorption band mentioned above, most of which are probably due to oxygen, this spectrum contains another item of interest, that is, a new absorption band for oxygen is shown beginning at λ 1000 and extending towards the shorter wave-lengths.

Figure 11.—Oxygen, disruptive discharge, 0.04 mm. pressure, circulation, 2 hours' exposure. Table V. Another type of discharge tube was used in obtaining this spectrum. This film is of especial interest because it extends the spectrum of oxygen to λ 507.2.[1] It also shows that the second absorption band of oxygen gradually fades away with reduced pressure. Even the first band, that is, that in the neighborhood of λ 1500 disappears rapidly as the pressure is reduced so that spectrum

[1] Some of these lines were found by Millikan and independently by the author by this distinctly different method.

lines begin to appear throughout its entire extent. It thus becomes evident that instead of oxygen being one of the most opaque gases in the Lyman region, it is perhaps one of the most transparent in the more

TABLE V.

Oxygen, Disruptive Discharge.

λ.	I.	Millikan, λ.	Lyman (Helium), λ.	λ.	I.	Lyman, λ.
507.2	1	507.8		946.1	3	
538.1	1			954.4	1	
554.2	1	554.2		962.8	2	
580.5	1			972.3	1	972.7
599.6	1	599.5	599.0	977.6	10	977.6
				980.2	3	
608.4	1			989.9	10	
610.0	1	610.1		991.5	10	
616.5	1	616.7		1000.0	3	
625.0	1	625.2		1006.4	1	
644.5	1	644.0	643.7	1010.5	11	
673.3	1			1026.0	5	
685.7	2			1028.6	2	
703.0	2	703.1	702.4	1037.0	10	
704.1	1		703.5	1040.6	1	
718.9	3	718.5	718.2	1041.8	1	
763.5	1			1066.3	5	
764.5	1			1085.2	10	
765.4	1			1110.3	2	
776.2	1			1103.7	1	
787.9	2			1114.4	1	
790.4	2			1122.9	1	
796.9	3			1128.4	5	
833.7	8		796.8	1129.6	2	
834.5	4	834.0	833.4	1130.4	2	
835.1	10		834.8	1132.5	2	
859.0	5			1134.8	10	
879.9	2			1139.0	2	
883.3	1			1142.0	2	
884.3	1			1144.1	3	
889.7	5			1147.4	4	
904.7	10		904.6	1149.2	1	
916.4				1149.8	1	
917.8	15			1151.3	1	
928.8	1			1152.6	6	
923.9	3			1153.9	2	

TABLE V.—*continued*.

λ.	I.	λ.	I.
1164.7	1	1265.1	1
1167. }	2	1267.7	1
1169.0 }	2	1269.8	1
1175.6	20	1272.6	1
1183.0	1	1275.6	2
1184.8	3	1277.5	4
1193.7	2	1280.7	1
1194.8	1	1286.6	1
1197.4	4	1288.7	1
1200.1	10	1290.3	1
1206.8	3	1295.1	1
1209.9	1	1296.9	1
1215.7	10	1299.2	1
1218.0	5		
1222.3 }	1		
1225.6 }	1		
12 0.6	2		
1239.1	4		
1243.0	3		
1247.7	10		

refrangible part of that region and in the beginning of the Millikan region. The table also gives, in parallel columns, the values of the wave-lengths found by the author in oxygen, those found by Millikan and attributed to oxygen, and those found by Lyman in helium. This experiment strengthens Millikan's assertion that the lines he observed are oxygen lines. Of course all the lines recorded in the table are not oxygen lines. Many are common to the spectrum of nitrogen, a few to the spectrum of hydrogen, and some arise from the impurities in the receiver. Still after the elimination of all of these, it is the opinion of the author, that there remain in the region between λ 800 and λ 1400 many strong oxygen lines.

Figure 12.—Oxygen, disruptive discharge, 0.02 mm. pressure, circulation, exposure 1 hour. It is hoped that this plate will show the short wave-lengths mentioned above better than Fig. 11. The spectrum is not as pure as the one described above.

Figure 13.—Oxygen, disruptive discharge, 0.001 mm. pressure, circulation, about 30 minutes' exposure. Table VI. In this experiment the mercury condensation pump was kept running and no attempt was made to keep the vapor out of the receiver and discharge tube. Since the pressure indicated above was read on a McLeod gauge, it represents the

TABLE VI.

Occurring in Oxygen with Mercury Vapor.

λ.	I.	Millikan, λ.
433.0	V.D.	
451.1	V.D.	
526.0	1	525.7
530.2	1	
533.5	1	
558.1	1	
574.5	1	
629.8	2	629.6
635.7	V.D.	
651.	1	
660.6		
671.8	3	
691.3	1	
747.5	2	
773.0	2	
788.1	1	

partial pressure of oxygen only. At this low pressure, many new lines were observed in the ultraviolet. These new lines are indicated in Table VI. Perhaps mercury and oxygen are the principal sources. Even a cursory examination of this plate shows that the lines near λ 600 are of intensity comparable with those of longer wave-length. This would indicate that in a strong discharge in oxygen these short waves are produced strongly with the rest, but of course are absorbed before they reach the plate.

Figure 14.—Oxygen, disruptive discharge, 1 cm. pressure, circulation, 15 minutes' exposure. This plate shows how transparent oxygen is in this region of transmission below its absorption band. Another plate was taken more recently at 2.5 cm. pressure, and 15 minutes' exposure. This latter shows practically the same lines as the above plate and with only slightly diminished intensity. Hence oxygen in layers of minimum thickness of 3.3 cm. has a narrow region of transmission, which includes the wave-lengths 1100 and 1217.7 Å. It has already been shown that nitrogen is equally transparent in this region in layers 4.5 cm. thick. Hence air has a remarkable transparency in this region of short wave-lengths, for if one uses as the basis of reckoning, the proportion of oxygen and nitrogen in the air, it is seen that the absorption equivalent of the above-mentioned thicknesses of oxygen and nitrogen when mixed in air is a layer 4.2 cm. thick. This fact recalls an observation of Lenard [1]

[1] Sitz. Heidelberg Akad. d. Wiss. Abhand., p. 31, 1910.

who detected a fluorescence about an aluminum spark in air that extended to a distance of 4 or 5 cm. from the source. The above-mentioned facts of the short waves of lengths 1100–1218 Å. being able to penetrate that thickness of air would explain the fluorescence. They probably are not the same rays that penetrated both quartz and fluorite as stated by him.

It gives the author great pleasure to acknowledge his indebtedness to his teacher Professor E. P. Lewis, by whose suggestion this research originated, and to express his thanks to his friend Professor R. T. Birge, for his many kind suggestions.

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THE VARIATION OF METALLIC CONDUCTIVITY WITH ELECTROSTATIC CHARGE.[1]

By F. Wenner, Nyna L. Forman, and A. R. Lindberg.

Synopsis.

Variation of Metallic Conductivity with Electrostatic Charge.—Last year Perkins reported a positive result. His experiment has been repeated, using a fine copper wire, 0.08 mm. in diameter, in series with a sensitive galvanometer, as the insulated secondary of a transformer. The galvanometer was found to read the same whether the potential of this wire was + 6,000 volts or − 6,000 volts with reference to the primary which was grounded. This *negative result* shows that the resistance of this wire is changed, if at all, by not more than one part in five million even when the potential gradient at the surface is raised to about 150,000 volts (root mean square value) per centimeter.

REFERRING to a paper by Professor H. A. Perkins, bearing the above title, we quote as follows from this journal, 18, p. 131, 1921.

"A simple conception of metallic conduction based upon moving electrons seems to justify the assumption that a negative charge should increase the conductivity of a circuit, and a positive charge should decrease it. This has been tested as follows: A primary coil of about 80 turns was wound upon a glass cylinder inside of which fitted a smaller cylinder similarly wound as a secondary. The primary was excited from a 60-cycle commercial circuit. The secondary circuit, carefully insulated throughout, included a moving coil galvanometer and was given an alternating charge from one terminal of a high tension transformer giving about 5,700 volts, the other terminal being grounded. The two coils wound upon glass acted as a condenser, so that a fairly large charge could be communicated to the insulated system.

"In operation the galvanometer was not affected by the charging potential, but the induced alternating current caused a slight vibration of the 'spot' on the scale, and if it reached too high a value (say 3 milliamperes) produced a small deflection always in the same direction, and due, probably to constriction of the helical portion of the suspension system. If, however, the induced current and the charging potential were both present, a deflection as high as 30 scale divisions was obtained, which indicated a direct current of about half a micro-ampere. This phenomenon behaved in a perfectly regular and definite manner, and

[1] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce.

reversed if the phase of the charging E.M.F. were reversed by interchanging the terminals of the transformer. A change of phase less than 180° produced proportional changes in the reading of the instrument."

An effect such as that just described would be of sufficient importance to require careful investigation and a modification of our notions of metallic conduction. However, before considering an investigation to establish quantitative relations justified, we thought it advisable to repeat the experiment to see whether or not we could observe an effect of the kind and order of magnitude claimed.

That our data might be comparable with that previously obtained, care was taken to use substantially the same test current and voltage. An exact duplication of conditions did not seem possible on account of the meagerness of the description, nor advisable on account of the possibility of introducing disturbing effects.

The test circuit was made up entirely of copper, and had a resistance of about 75 ohms. Of this about 60 ohms was of wire having a diameter of .08 mm. and so disposed as to receive very nearly the same surface charge as if straight and at a considerable distance from other conductors. This wire was silk-covered, but presumably this did not materially affect the results obtained. This circuit was electrically shielded at all points of mechanical support. The shield included the case of the galvanometer and the metal covering over the secondary winding of the transformer supplying the test current, both insulated from the circuit. The shield and the test circuit were electrically connected through two 20-watt, 125-volt carbon lamps symmetrically located with respect to the galvanometer so that the shield and the test circuit were always at substantially the same potential with respect to "ground." Only by this or a similar arrangement was it thought practicable to secure an effective insulation for the test circuit. The transformer supplying the test current had oil and glass insulation between the primary and secondary windings and a shield for the primary winding as well as for the secondary winding. The shield for the primary winding was connected to "ground." Inside the secondary winding and extending to a considerable distance beyond the ends was a laminated iron core, the outer laminations of which formed a part of the shield around the secondary winding. With this double shield, and glass and oil insulation, we have reason to think there was no appreciable change either in the conduction or the displacement current from one winding to the other, with changes in the phase between the current in and the voltage of the test circuit. The transformer supplying the voltage to the test circuit was a 5,500- to 110- volt, 40- to 80-cycle potential transformer. The 110-volt winding

was connected to our 120-volt, 60-cycle power circuit, while one terminal of the 5,500-volt winding was connected to ground and the other to the shield of the test circuit.

Current for the test circuit was supplied from a small 60-cycle generator located in the laboratory and under the control of one of the observers. The test current was delivered from this generator to the test circuit by two transformers and regulated mainly by an inductance between the generator and the first transformer, which was of a commercial type. The second transformer was the one described above. The test current was approximately 2×10^{-3} ampere, and the sensitivity of the galvanometer was such that a change of 10^{-9} ampere gave a change in the deflection of 1.2 scale divisions. During the observations, conditions usually were sufficiently constant so that the deflection of the galvanometer could be read to about half a scale division.

As a result of the alternating current there was a broadening of the image amounting to 20 scale divisions and always a shift of the position of this band with respect to the position of the image when there was no alternating current in the circuit. This deflection was made small by making the "zero" correspond approximately with the position towards which the image moved as the result of the dynamometer action between the current in the coil and the current induced in the pole pieces and core. When 6,000 volts were applied to the test circuit there was regularly a quick motion of the coil amounting to about ten scale divisions, and then a return to zero in a time corresponding to the deflection period of the galvanometer. The reason for this was not obvious, but as it in no way interfered with the observations, we saw no reason for being especially concerned about it. A sectored disk on the fly wheel of the generator, illuminated by a metal filament lamp connected to the power system, furnished a stroboscopic means of showing relative changes in the phase of the current in and the voltage of the test circuit.

During the experiment the generator supplying the test current was run just slightly above or just slightly below synchronism with the power circuit so that there was a gradual shift in the phase between the voltage of and current in the test circuit. During the observations, usually the time required for a shift of one cycle was between 5 and 10 seconds or approximately the same as a free period of the galvanometer.

Observations consisted in noting changes in the phase and looking for corresponding changes in the deflection of the galvanometer. However, no changes in the deflection of the galvanometer, that is of the band image, corresponding with changes in the phase could be detected.

If, therefore, the observations are reliable, we may conclude that when the potential of a practically straight, .08 mm. diameter, copper wire, is changed from + 6,000 volts to − 6,000 volts, its resistance is changed, if at all, by not more than about one part in 5 million, or not more than two-tenths per cent. of that reported for the original experiment.

While the two experiments probably differ considerably in detail, they seem to be fundamentally the same. There should, however, have been a difference in the magnitude of the effect observed if the explanation given is correct, for the following reason. In the original experiment only that part of the test circuit having a small part of the resistance was so disposed that it could have had a high potential gradient at the surface, and that, for the most part, only on one side of the wire, which presumably was larger than .08 mm. in diameter. In our experiment the potential gradient at the surface of the .08 mm. diameter wire was about 150,000 volts (root mean square value) per centimeter. The surface charge was therefore about as large as could have been obtained in air without special precautions, with reasonable assurance that there was no corona, and this density was maintained over a part of the circuit having more than three-fourths of the total resistance. It seems therefore that we should have observed an effect larger possibly by a factor of the order of ten. Inasmuch as the effect if present at all in our experiment certainly was smaller by a factor of more than 500, we may conclude that quantitatively the results of the two experiments differ by a factor of more than 1,000. Since both experiments gave definite results, it seems that the cause or causes for this difference should have been evident. However, of the causes considered, none which seemed plausible should have escaped notice in either experiment. We therefore have no explanation to offer for the marked difference in the results obtained.

A limited experience with the apparatus used, some of which was not well suited to the purpose, and all of which was hastily assembled, leads us to think that by this method it should be possible to detect changes in the direct component of the current to better than one part in 5 million of the alternating current. Steadiness of conditions could be much improved by the use of more suitable sources of current and voltage, and by working at night or when heavy machinery is not in operation in the vicinity. The sensitivity might be increased or a larger test current used if a galvanometer better adapted to this purpose were employed. Further, by avoiding all points and sharp bends, the potential gradient over that part of the circuit having most of the resistance could be made somewhat larger without getting into serious difficulties on account of

corona. Considering all factors which limit the accuracy of the observations it seems that an overall precision ten times that which we claim for our experiment might be realized. However, unless a plausible explanation is found for the negative results which we obtained, or the matter becomes of more importance than it seems to be at the present time, we do not think that we would be justified in attempting a greater refinement.

Department of Commerce,
Bureau of Standards,
Washington, D. C.,
June, 1922.

Note.—A copy of this paper was sent to Professor Perkins, who in reply states that he has found the cause for the large effect originally reported, and expects to publish soon a paper giving the results obtained in a more recent investigation.

RECIPROCAL DIFFRACTION RELATIONS BETWEEN CIRCULAR AND ELLIPTICAL PLATES.

BY JOHN COULSON AND G. G. BECKNELL.

SYNOPSIS.

Diffraction Patterns inside Elliptical Shadows Due to a Point Source of Light.—When a circular disc with its plane originally tangent to the light wave is rotated about an axis in its plane, the Arago spot changes to a figure with four cusps which move out along the axes of the elliptical shadow, two approaching the foci as limits and the other two going outside the shadow. These changes are shown by a set of photographs obtained with a disc 1.6 cm. diameter placed 2 meters from a pin-hole 0.3 mm. in diameter and 5 meters from the photographic plate. The diffraction pattern was found to depend only on the ellipticity of the shadow whether produced by an ellipse or by an inclined disc. Each quadrant of the diffraction pattern was found to be associated with the quadrant of the shadow adjacent to it but on the opposite side of the major axis. Careful measurements of the photographs proves that in each case the diffraction pattern is the *evolute of the geometrical shadow*. The effect is as though each element of the edge of the shadow contributed a spot along its normal, the result being a *caustic curve of diffraction*.

INTRODUCTION.

EARLY in the nineteenth century Poisson[1] predicted that if the Huyghens-Fresnel theory was correct the light intensity behind the center of a small opaque disc illuminated by a point source should be about the same as though the disc were removed. Arago verified this experimentally using a disc about 2 mm. in diameter. In a later paper Arago states that the same phenomenon was discovered by Delisle in 1715.

Some of the more recent investigators, Croft, Arkadiew, and Hufford[2] have repeated and extended the work of Arago. However, none of the writers has drawn attention to the fact that a disc illuminated by a point source of light and placed perpendicular to the wave-normal, when gradually rotated about an axis in its own plane produces a succession of broadening diamond-like figures with concave sides; nor, have they drawn attention to the reciprocal figures produced by ellipses.

[1] Poisson, Verdet, Leçons d'Opt. Phys., Vol. 1, Sect. 66.
Arago, Oeuvres Complètes, Vol. VII., p. 1.
Delisle, Mém. de l'anc. Acad. des Sciences, 1715, p. 166.

[2] Croft, W. B., Phil. Mag., Vol. 38, p. 70 (1894); Nature, Vol. 66, p. 354 (1902).
Arkadiew, W., Phys. Zeit., Vol. 14, p. 832 (1913).
Hufford, PHYS. REV., Vol. III., p. 241 (1914); Vol. VII., p. 545 (1916).

APPARATUS AND METHOD.

The discs were turned from brass, the edges beveled and then polished while on the lathe with a fine-grained oil-stone. The sizes ranged from .5 cm. in diameter to over 5 cm.

Very accurate ellipses were produced by a lathe method as follows: A circular cylinder of brass was sawed in two along a plane making the desired angle with its axis. A thin plate of hard-rolled copper was fastened between the sections of the cylinder by means of screws inserted from one end of the cylinder. The cylinder was then chucked in a lathe and turned down so that the minor axis of the elliptical section was equal to the diameter of the circle mentioned above. This elliptical section having been replaced by another sheet of the same material the cylinder was further turned down to such size that the major axis of the new ellipse was equal to the diameter of the disc.

Each of these plates was held at the center of a circular ring (about 20 cm. in diameter) by three No. 44 steel wires. This ring was fitted inside a second ring of slightly larger diameter, so as to slide into any position in its plane. The outer ring was mounted in such a manner as to permit of rotation about a horizontal axis as well as about a vertical axis. By means of clamping screws rotation about any one of the three axes could be made without disturbing the other two adjustments.

The mounted disc was placed in the path of a cone of light emanating from a pinhole source illuminated from behind by a self-regulating carbon arc and a system of condensing lenses. The shadow of the disc was received through a long tube, blackened inside, upon a photographic plate.

The distance between the photographic plate and pinhole was 7 meters, and that between pinhole and disc was 2 meters. The photographic reproductions shown here were produced by a pinhole about .3 mm. in diameter, and were made with a disc 1.6 cm. in diameter and with two ellipses, one having its major axis equal to the minor axis of the other and equal to the diameter of the disc.

PROCEDURE.

The disc was adjusted until the Arago spot was sharply defined at the center of the circular shadow received at the position of the photographic plate. In this position the disc is perpendicular to the wave-normal. The sizes of the Arago spot and the circular shadow are indicated by No. 1, Plate I.

When the disc is rotated about an axis in its own plane, in this case a vertical axis, the Arago spot changes gradually into the series of expanding patterns mentioned before. These are illustrated by Plate I,

Nos. 2 to 8, corresponding to angles of rotation of 10°, 15°, 22.5°, 30°, 37.5°, 45°, and 60° respectively. Any one of these figures may be duplicated by an ellipse, whose minor axis equals the diameter of the disc, cut from a circular cylinder at the corresponding angle and placed perpendicular to the wave-normal.

Plate I., No. 9 was produced by an elliptical plate cut at an angle of 37.5°, and placed in the normal position just described. It corresponds to No. 6 for the disc when turned through an angle of 37.5°. In this case the major axis of the ellipse is equal to the diameter of the disc. An ellipse similarly cut, but with its minor axis equal to the diameter of the disc, when placed perpendicular to the wave-normal produces Plate II., No. 10. It will be seen that this diffraction pattern corresponds in shape to that of Plate I., No. 9, and is proportional in size to the dimensions of the ellipse.

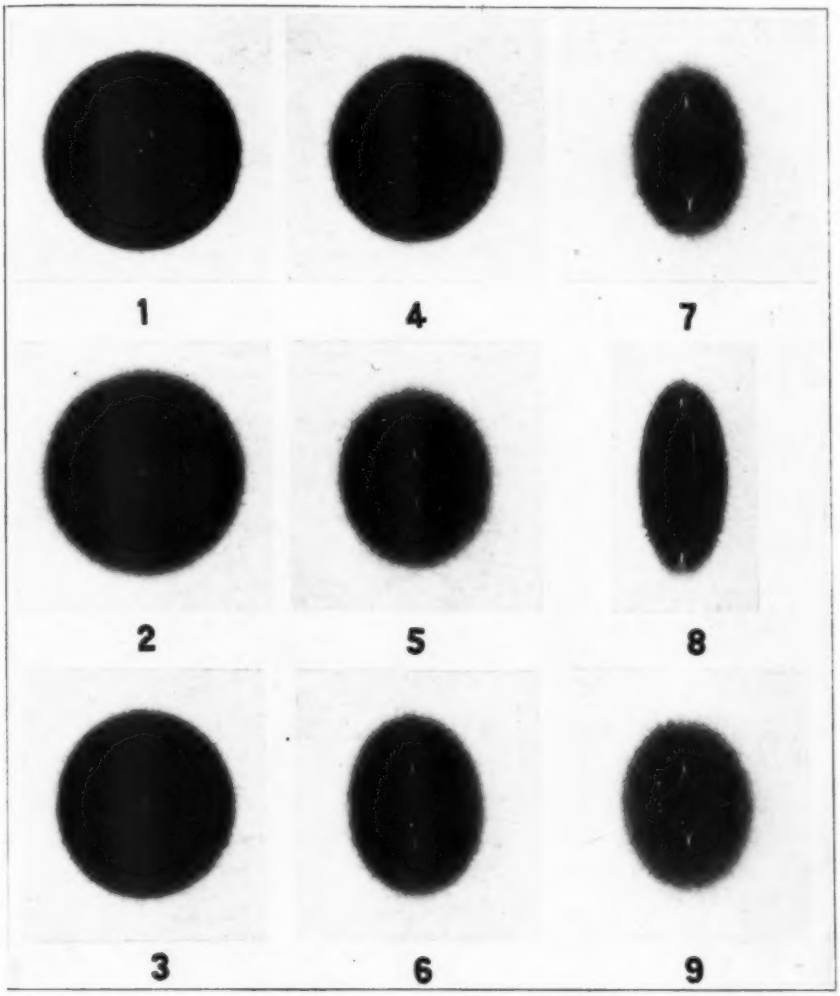
When this ellipse is rotated about an axis in its own plane until the shadow produced is a circle (in this case 37.5°) then the Arago spot appears at the center of the shadow, as shown in Plate II., No. 11.

Examination will show that in all cases where the four cusps of the diffraction figure appear within the shadow (Nos. 3, 4, 5, 6, and Nos. 9 and 10) the intensity of light is greatest at the cusps lying on the major axis of the elliptical shadow. This fact is important in the experimental analysis, an account of which is now to follow.

Plate II., No. 16, shows the diffraction pattern produced by an ellipse when a straight-edge in the same plane is made tangent to the ellipse at the end of the major axis, the plane of the ellipse being perpendicular to the wave-normal. The spear-like shadow cast from the point of tangency is directed to the *adjacent* cusp. But, if the straight-edge is made tangent at the end of the minor axis the pointed shadow is directed to the cusp lying on the *opposite* side of the major axis. This is shown by Plate II., No. 17.

From the last two illustrations it is evident that each cusp lying on the major axis is produced by light emanating from the neighborhood of the *nearer* end of the same axis of the elliptical plate; while each of the cusps on the minor axis is due to light coming from the *farther* end of the latter axis. Furthermore, it has been observed that if the straight-edge is made tangent at successive points of the ellipse lying between the ends of the major and minor axes the extremity of the pointed shadow moves along the four-cusped diffraction figure. At any definite position of the straight-edge the bisector of the angle at the tip of the shadow is tangent to the diffraction figure and normal to the geometrical shadow.

If a circle replaces the ellipse the shadow from the point of tangency is directed toward the Arago spot at the center of the circular shadow.



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(See No. 18.) If the disc and straight-edge be now rotated about an axis in their plane figures like Plate II., No. 16 and No. 17 are produced.

Attention may be drawn to the fact that the diffraction bands resulting from any combination of ellipse and tangent straight-edge differ in nature from the quadrantal diffraction figure produced by the ellipse alone. In the case of the former the bands are fringed with the prismatic colors, while in the latter case this color separation does not take place. It appears, also, upon photographing these figures with light of different colors that the dimensions of the main figures are independent of the wave-length.

Photographs 12, 13, 14, and 15 were taken while light was excluded from certain quadrants of an ellipse placed perpendicular to the wave-normal. In No. 13, an opaque screen shuts off all of the ellipse on one side of the major axis. Here the diffraction pattern lies *inside* the shadow of the screen. Hence, it is produced by the light coming from the *opposite* side of the major axis. If, now, the screen is so placed as to exclude light from all of the ellipse on one side of the minor axis the resulting pattern falls *outside* the shadow of the screen. Here, on the contrary, the light producing the diffraction comes from the *same* half of the ellipse into which the pattern falls. (See No. 14.)

Shutting off the illumination from two diagonally opposite quadrants of the ellipse produces the effect shown in No. 12. It will be observed that half of the complete diffraction figure is missing, and that the cusps do not appear. Furthermore, the portion of the figure lying in either quadrant is due to light from an adjacent quadrant, and not from the one diagonally opposite.

No. 15 completes the analysis concerning each quarter of the diffraction figure and the illuminated quadrant which produces it. Here the major axis of the ellipse stands lengthwise of the page, as it does in the other illustrations. In terms of the usual trigonometric convention light is excluded from all but the first quadrant of the elliptical plate, and the resulting diffraction is seen to lie only in the second quadrant of the geometrical shadow. This shows that each illuminated quadrant produces independently its own quarter of the diffraction figure and, therefore, that each of these quarters is due to light from its corresponding *adjacent* quadrant with respect to the major axis. Exactly similar properties are found in the case of the circle rotated through an angle.

The foregoing results may be summarized as follows:

1. The diffraction figures are quadrantal and symmetrical. As the eccentricity of the elliptical shadow gradually increases the cusps which lie upon the minor axis recede indefinitely, while those on the major axis

always lie within the shadow. As the eccentricity approaches zero the figure degenerates into a circular spot which becomes a geometrical point for a point source of light.

2. Each quarter of the diffraction figure is produced by light from the adjacent quadrant with respect to the *major* axis.

3. The intensity of illumination of the cusps lying on the major axis is always greater than that of those lying on the minor axis.

The facts here enumerated have suggested that the diffraction figures are the *evolutes* of an ellipse.

The evolute of a given curve is defined as the locus of its center of curvature. Every normal to the given curve is tangent to its evolute; hence, the evolute is the envelope of these normals.

In the case of an ellipse the cusps of the evolute which lie on the minor axis recede indefinitely with increasing eccentricity of the ellipse, while those on the major axis at the same time approach the foci. With decreasing eccentricity the evolute contracts and, in the limit, becomes a geometrical point. Furthermore, the envelope of the normals from any quadrant of the ellipse is the adjacent quarter of its evolute with respect to the *major* axis. Such an envelope corresponds to the curve formed by the rays as mentioned above.

The difference in the brightness of pairs of opposite cusps is accounted for if we consider the distance from the end of the major axis to the nearest cusp of the evolute, and the distance from the end of the minor axis to the further cusp on that axis. These distances are b^2/a and a^2/b respectively, where a and b are the major and minor semi-axes of the ellipse. Here b^2/a is always less than a^2/b. The distances just mentioned are, also, the radii of curvature of the ellipse at the ends of the major and minor axes.

The equation of the evolute corresponding to the ellipse

$$(x/a)^2 + (y/b)^2 = 1,$$

is

$$(ax)^{2/3} + (by)^{2/3} = (a^2 - b^2)^{2/3}.$$

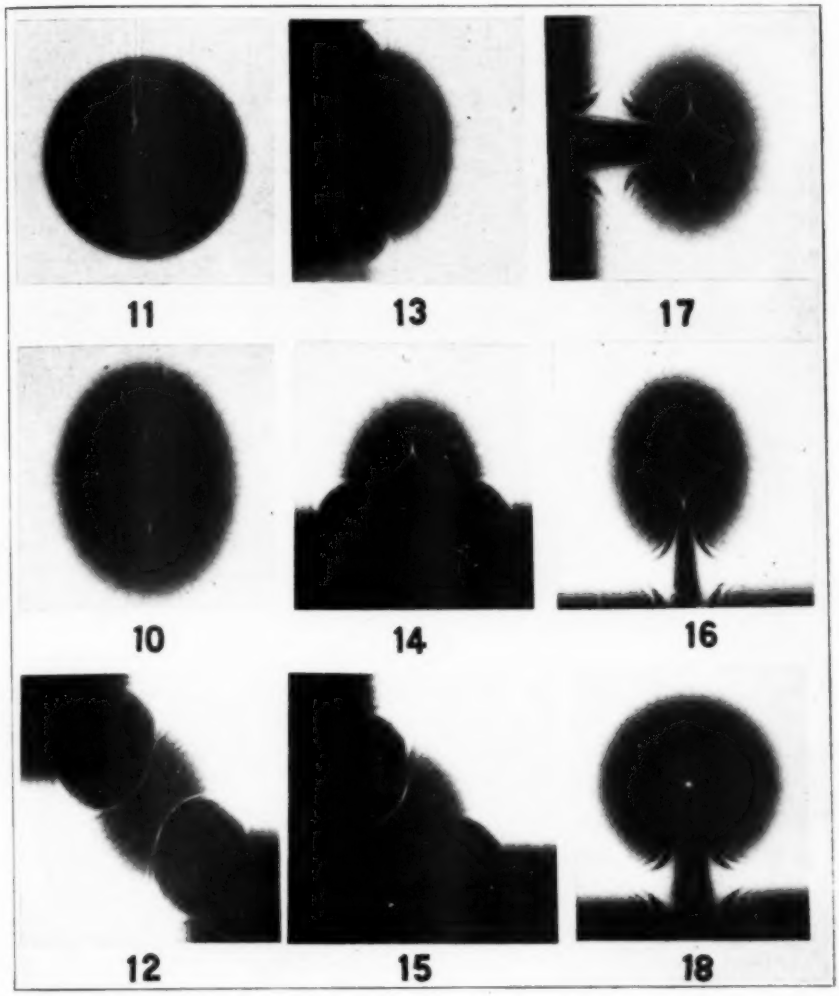
The respective distances between the cusps lying on the major axis and those lying on the minor axis are:

$$2x_0 = 2(a^2 - b^2)/a,$$

and

$$2y_0 = 2(a^2 - b^2)/b.$$

These distances when taken from the photographs permitted the calculation of a and b, which in every case were found to be the dimensions of the corresponding geometrical shadow.



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In order to show the complete coincidence between the diffraction figure and the evolute of the geometrical shadow it was necessary to produce photographically a large sharp-lined figure. This was done by using a disc of large diameter (5.11 cm.) and a very small pinhole source (.12 mm.). The disc was rotated 37.5° with respect to the wave-normal. The figure thus produced, which was about 7 by 8 cm., was projected optically, with a magnification of about 8 diameters, upon a sheet of coördinate paper. The values of x and y for one quadrant of this sharply outlined figure are the points represented by circles in Fig. 19.

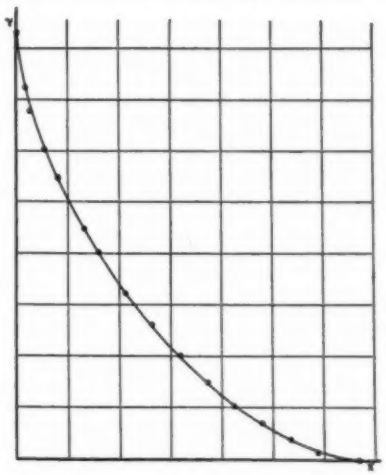


Fig. 19.

The curve itself is the computed evolute of the elliptical shadow. The agreement is well within the limits of observation.

The identity of the diffraction figure and the evolute of the geometrical shadow may be shown more readily from the following property of the evolute. The difference between the radii of curvature at any two points in the same quadrant of an ellipse is equal to the arc cut off of its evolute by the normals to the ellipse at the given points. Hence, it may be proved that the length of the quadrant of the evolute is equal to $(a^3 - b^3)/ab$.

The length of the quadrant of the evolute was measured for several figures (after enlargement) by rolling a self-recording wheel along the periphery of the curve. A planimeter-wheel was used for this purpose. The agreement between the length of the quadrant of the evolute thus measured and the quantity $(a^3 - b^3)/ab$ for the corresponding geometrical shadow was in each case less than one per cent.

The agreement between the diffraction figures produced by an ellipse and a rotated circle casting the same geometrical shadow is shown in

the table. These data were taken from Plate II., No. 6, and No. 9, enlarged.

x.	y (Observed).	
	Rotated Circle.	Ellipse.
.000	1.330	1.340
.056	1.035	1.038
.127	.875	.851
.190	.720	.735
.253	.615	.631
.380	.445	.455
.507	.300	.314
.633	.197	.200
.760	.108	.108
.887	.044	.041
1.032	.006	.000
1.050	.000	

Attention may be called again to one of the important properties of the evolute. That is, the evolute is the *envelope of the normals* of the corresponding curve producing it. In the experiment with the straight-edge tangent to the elliptical plate it has been shown that for any given position of the straight-edge the median line of the corresponding pointed shadow is tangential to the diffraction figure and normal to the geometrical shadow of the plate. Hence, we may conclude that these diffraction figures constitute a family of envelopes, and corresponding to the caustics of reflection and refraction, that the figures here shown are the *caustics of diffraction*.

UNIVERSITY OF PITTSBURGH,
May, 1922.

HEAT FLOW IN A FINITE CYLINDER HAVING VARIABLE SURFACE TEMPERATURE.

BY GEORGE E. THOMPSON.

SYNOPSIS.

Equations of heat flow into finite circular cylinders when the surface temperature is changed either suddenly or at a uniform rate, are derived. In the first case the surface temperature of a cylinder whose temperature is initially uniform throughout is suddenly changed from 0 to V_0, kept there for a certain time and then suddenly changed to V_2 and kept there indefinitely. In the second case the surface temperature is changed to V_0, then is increased at a uniform rate from V_0 to V_2 and then is kept constant indefinitely. These two cases correspond roughly to the *changes occurring in two canning processes* and the theoretical curve for case two is found to agree roughly with an experimental curve obtained with a pint Mason jar filled with spinach by the "cold-pack" method.

SOME time ago the author of this paper[1] made a comparison of theoretical and experimental temperature-time curves for the flow of heat into finite circular cylinders—the cylinders under experimental test being cans of fruit or vegetables in the sterilizing process. The theoretical derivations of the formulæ for heat flow were not given in the published results at that time. Two formulæ not previously worked out were used. It is the purpose of this paper to present the derivation of these formulæ.

The two new cases worked out are as follows: In the first case the surface of the cylinder is maintained constant for a given length of time and then suddenly changed to a new value which is kept constant indefinitely. The initial temperature of the cylinder is considered uniform throughout. This corresponds to the conditions which are sometimes approximately maintained in a certain canning process—namely, where the can is heated in a bath of medium temperature for a limited time to expel the air and then, after sealing, is placed in a steam bath at sterilizing temperature. The second case considered corresponds closely to the conditions which apply to "cold-pack" canning methods. The surface temperature is assumed to increase linearly from a medium temperature to the sterilizing temperature and remain constant thereafter, the interior temperature being initially uniform throughout. We shall refer to these problems as Case I. and Case II.

Case I.—Let us use cylindrical coördinates, z representing the distance of any point from the center of the cylinder along the axis; r, the per-

[1] Thompson, Journ. Ind. and Eng. Chem., July, 1919.

pendicular distance of the point from the axis; l, the half length of the cylinder, and a, its radius. Only right circular cylinders will be considered.

The problem, then, is to find a solution of the partial differential equation:

$$\frac{\partial v}{\partial t} = k\left(\frac{\partial^2 v}{\partial r^2} + \frac{1}{r}\frac{\partial v}{\partial r} + \frac{\partial^2 v}{\partial z^2}\right) \tag{1}$$

subject to the conditions

(*a*) $v = v_0$ at $r = a$, $z = \pm l$ for $t < t_1$
(*b*) $v = 0$ at all points in the cylinder when $t = 0$
(*c*) $v = v_2$ at $r = a$, $z = \pm l$ or $t \gtrless t_1$.

In the above expressions, v is the variable interior temperature; t, the time; and k, the diffusivity of the material constituting the cylinder.

We have to get the solution of the problem in two parts; first for $t < t_1$ and then for $t > t_1$. Carslaw has included the general solution for a steady surface temperature in his textbook, Fourier Series and Integrals, p. 324. This solution making $n = 0$ for symmetrical distribution is as given in Equation (3) where

$$A_{\mu,\,m} = \frac{2\int_0^a J_0(\mu r)r\,dr\int_{-l}^{+l}\sin\frac{m\pi}{2l}(z+l)dz\int_{-\pi}^{+\pi}f(r,\,\theta,\,z)d\theta}{\pi a^2 l J_1^2(\mu a)}. \tag{2}$$[1]

By putting $n = 0$ since the distribution is symmetrical and $f(r, \theta, z) = 1$, this solution when modified to correspond to the conditions of our problem becomes for $t = t_1$,

$$v = -\sum_{\mu}\sum_{m=1}^{\infty} A_{\mu,\,m}v_0 e^{-Rt_1}J_0(\mu r)\,\sin\frac{m\pi}{2l}(z+l), \tag{3}$$

where μ is a root of $J_0(\mu a) = 0$ and m is any integer,

$$R = k\left(\mu^2 + \frac{m^2\pi^2}{4l^2}\right),$$

and

$$A_{\mu,\,m} = \frac{1}{2}\cdot\frac{8(1-\cos m\pi)l}{\pi a^2 m l J_1^2(\mu a)}\int_0^a J_0(\mu r)r\,dr, \tag{4}$$

where $\int_0^a rJ_0(\mu r)dr$ may be replaced by its value $(a/\mu)J_1(\mu a)$.

In the second part of the problem where $t > t_1$ we have to solve the same differential equation subject to Condition (*c*) and that the interior temperature at $t = t_1$ is given by Equation (3). In order that the

[1] Note that a factor, r, is omitted in the first integral of this expression in Carslaw's book; also b is a misprint for l in the denominator.

surface temperature may still be considered zero we shift the temperature scale by the amount $(v_2 - v_0)$ and get for the interior temperature distribution at $t = t_1$ the expression

$$f(r_1 z) = -(v_2 - v_0) - \sum_{\mu} \sum_{m=1}^{\infty} A_{\mu,\, m} v_0 e^{-Rt_1} J_0(\mu r) \sin \frac{m\pi}{2l}(z + l). \qquad (5)$$

By substituting this value of $f(r, z)$ in the expression at bottom of page 324 of Carslaw's textbook, we get, after simplifying,

$$A_{\mu,\, m}' = \frac{4(v_2 - v_0)(\cos m\pi - 1)}{m\pi(\mu a) J_1(\mu a)} - A_{\mu,\, m} v_0 e^{-Rt_1}, \qquad (6)$$

$$= -A_{\mu,\, m}(v_0 e^{-Rt_1} + v_2 - v_0). \qquad (7)$$

Hence we have

$$V' = \sum_{\mu} \sum_{m=1}^{\infty} A_{\mu,\, m}' e^{-R(t-t_1)} J_0(\mu r) \sin \frac{m\pi}{2l}(z + l). \qquad (8)$$

We should now increase all temperatures in (3) by v_0 and in (8) by v_2 in order to get the results into their final forms.

Case II.—As in Case I. we have to solve this problem in two parts; the first part to correspond to the condition that the surface temperature increases linearly with t until $t = t_1$. In the second part the surface temperature remains constant at a value v_2. Then

(*d*) $v = v_0 + Bt$ at $r = a$ and $z = \pm l$ when $t < t_1$,
(*e*) $v = v_2 = v_0 + Bt_1$ at $r = a$ and $z = \pm l$ when $t \gtrless t_1$,
(*f*) and $v = 0$ for all points in the cylinder when $t = 0$.

Duhamel has given a theorem (Carslaw, loc. cit., p. 208) by means of which the solution for a variable surface temperature can be deduced from the solution for a steady surface temperature. According to this rule we are to use the solution which is given in equation (3) for a surface temperature maintained at zero. We are to replace the t in the surface-temperature function by λ and in the body temperature by $t - \lambda$. If the surface temperature be maintained at zero we have, after applying Duhamel's rule

$$V = (v_0 + B\lambda)[1 - v(t - \lambda, r, z)], \qquad (9)$$

where V is the function wihch is to be differentiated with respect to t and integrated with regard to λ between the limits 0 and t; and v is the function given in Equation (3) after $t - \lambda$ has been substituted for t.

The t-differentiation gives

$$\frac{\partial V}{\partial t} = (v_0 + B\lambda) \sum_{\mu} \sum_{m=1}^{\infty} R A_{\mu,\, m} e^{-R(t-\lambda)} J_0(\mu r) \sin \frac{m\pi}{2l}(z + l). \qquad (10)$$

After factoring (10) and integrating with regard to λ that part involving λ we have, after recombining,

$$V' = \sum_{\mu} \sum_{m=1}^{\infty} A_{\mu,m} \left[v_0(1 - e^{-Rt}) + B\left(t - \frac{1 - e^{-Rt}}{R} \right) \right] J_0(\mu r) \sin \frac{m\pi}{2l} (z + l), \tag{11}$$

$$= v_0 + Bt - \sum_{\mu} \sum_{m=1}^{\infty} A_{\mu\ m} \left[v_0 e^{-Rt} + \frac{B}{R}(1 - e^{Rt}) \right] J_0(\mu r) \sin \frac{m\pi}{2l} (z + l). \tag{12}$$

The coefficient of $v_0 + Bt$ is shown to be unity by placing $v = 1$ and $t = 0$ in equation (3). V' represents the interior temperature between $t = 0$ and $t = t_1$. After the surface temperature becomes constant at $t = t_1$ we have to solve another problem with V' as initial interior temperature and surface temperature $v_2 = v_0 + Bt_1$. In order to use the expression given by Carslaw (p. 324) we must reduce all temperatures by an amount $v_0 + Bt_1$ so as to make the surface temperature zero. The final result will then have to be increased by this amount. Substituting in Equation (2), $f(r, \theta, z) = V' - v_0 - Bt_1$ we get

$$2\pi C_m \int_{-l}^{+l} \sin^2 \frac{m\pi}{2l} (z + l) dz = 2\pi C_m l, \tag{13}$$

since the z-integration gives only one term, the others being equal to zero. C_m is used for the expression

$$- \sum_{\mu} \sum_{m=1}^{\infty} A_{\mu,\ m} \left[v_0 e^{-Rt_1} + \frac{B}{R}(1 - e^{-Rt_1}) \right] J_0(\mu r). \tag{14}$$

We get, therefore,

$$A_{\mu,\ m}' = \frac{- 2\pi A_{\mu,\ m} \left[v_0 e^{-Rt_1} + \frac{B}{R}(1 - e^{-Rt_1}) \right] \int_0^a J_0(\mu r) r\, dr}{\pi a^2 J_1^2(\mu a)}. \tag{15}$$

Putting

$$\int_0^a J_0^2(\mu a) r\, dr = \tfrac{1}{2} a^2 J_1^2(\mu a)$$

and putting this value of $A_{\mu,m}'$ as the constant of Equation (3) we have the solution for $t > t_1$ as follows:

$$V'' = v_0 + Bt_1 - \sum_{\mu} \sum_{m=1}^{\infty} A_{\mu,\ m} \left[v_0 e^{-Rt_1} + \frac{B}{R}(1 - e^{-Rt_1}) \right] e^{-R(t - t_1)} J_0(\mu r) \sin \frac{m\pi}{2l} (z + l). \tag{16}$$

The convergence of this series is greatly helped by the fact that the terms are alternately plus and minus.

Figure 1 shows a theoretical and an experimental curve for Case II.

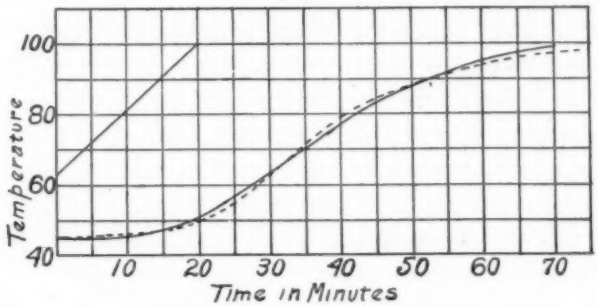


Fig. 1.

The broken line is the theoretical and the full line the experimental curve, both referring to temperatures at the center of the cylinder. The surface temperature was about 63° C. initially and increased to 100° C. in twenty minutes, remaining constant thereafter. The cylinder in this case was a pint Mason fruit jar filled with spinach as it is ordinarily canned. The agreement between the two curves is satisfactory when it is remembered that the experimental conditions approximate only roughly to the theoretical conditions. In practice the diffusivity increases with temperature while it was assumed constant in plotting the theoretical curve.

In order to show how the variations of surface temperature modify the rate of heating the curves of Fig. 2 have been plotted, using arbitrary

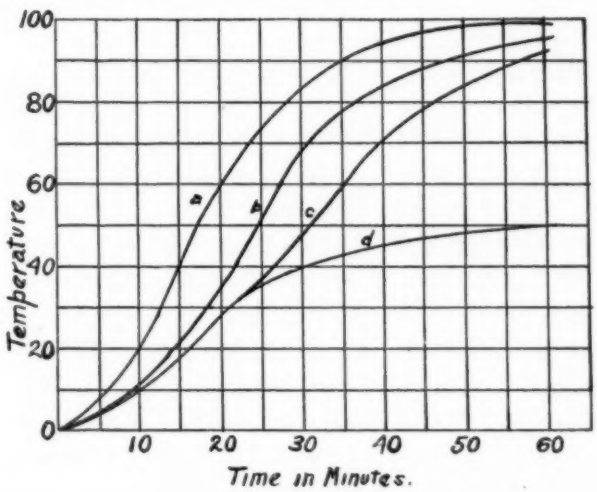


Fig. 2.

values for the constants of the equations. The curves plotted apply to the center of the cylinders only. Curve *a* is computed from Equation 3. The initial interior temperature of the cylinder is 0° C. throughout and the bath is maintained at 100° C. from the beginning. Curve *b* is computed from Equations 12 and 16. The conditions are the same as in Curve *a*, except that the surface temperature varies uniformly from 50° C. to 100° C., reaching the latter value after 20 minutes and remaining constant thereafter. Curve *c* is computed from Equations 3 and 8. The surface temperature is maintained at 50° C. for 20 minutes and then suddenly increased to 100° C. and maintained at this temperature indefinitely. Curve *d* is computed from Equation 3, the surface temperature being 50° C. continuously from the beginning.

The author desires to express his indebtedness to the late Professor James MacMahon of Ithaca, N. Y., for the solution of the equations given under Case II.

PHYSICS DEPARTMENT,
IOWA STATE COLLEGE,
AMES, IOWA,
May, 1922.

AN EXTENSION OF THE PRINCIPLE OF THE DIFFRACTION EVOLUTE, AND SOME OF ITS STRUCTURAL DETAIL.

By G. G. Becknell and John Coulson.

Synopsis.

Diffraction Patterns inside Shadows due to Point Sources of Light.—(1) *Conic section shadows.* In confirmation and continuation of the results in the preceding article, the patterns are found to depend only on the shape of the shadow, the Arago spot being obtained at the center of the circular shadow even when this was cast by a spiral edge of large pitch ground to the form of a truncated cone, when the point source was placed at the apex. Patterns inside the shadows of hyperbolic and parabolic plates were also obtained and are reproduced. As in the case of the ellipse, the predominant figure in each case is the evolute of the edge of the shadow. (2) *This general relation between diffraction caustic and shadow* is found to hold even in the case of the *shadow of the involute of a circle*, when the diffraction figure was identical with the generating circle which was, of course, the evolute of the edge of the shadow. A series of photographs of elliptical shadows show that the diffraction caustics are not continuous curves. The changes of detail and of color in the patterns with change of ellipticity of the shadow are described at some length.

IN a previous paper[1] reported in this journal it was shown that for circular and ellipitcal plates illuminated by a point source, whatever the position of the plates with reference to the wave-normal, a predominant figure was produced behind the object which proved to be the evolute of the geometrical shadow.

Knowing the general mathematical relations between plane curves and their evolutes, it did not seem probable that the example there discussed of the relation between an elliptical shadow and its diffraction figure could be merely an isolated case of a curve and its evolute. This paper presents illustrations of diffraction patterns produced by parabolas, hyperbolas, and other diffracting objects.

Accurate parabolic and hyperbolic plates were produced by a lathe method similar to that discussed in our former paper for elliptical plates. In this case a cone was used instead of a cylinder. By holding thin plates of metal between proper sections of the cone it was possible to turn out both shapes at one operation. However, in the case of the parabola it was necessary that the cone be sliced well back from the apex. Otherwise, the bevelled edge of the plate caused the shadow to be that of two overlapping parabolas. It is also worth noting that it is far more difficult to turn out a true parabola than a true hyperbola since the para-

[1] See page 594, this issue.

bolic section must be accurately parallel to the generator of the cone. Much of the success in producing these plates is due to the careful workmanship of Mr. G. S. Shallenberger, our department mechanician.

The apparatus and its arrangement were the same as used previously. The diffracting plates were supported on a rod extending along the axis of symmetry of the figure in such a way as not to interfere with the diffraction pattern. The plates were then oriented until the patterns were symmetrical with respect to the axis just mentioned.

Plate I., No. 1, shows the shadow and diffraction within the shadow of a hyperbolic plate whose height along the axis was 1.85 cm., and whose base was 3.6 cm. No. 2 shows the corresponding photograph for a parabola of height 2.7 cm., base 2.4 cm. The curves are precisely the ones anticipated, and measurements taken from the plates prove them to be true evolutes.

The equation of the hyperbola referred to its vertex is

$$(x/a)^2 + 2(x/a) - (y/b)^2 = 0.$$

And the equation of the corresponding evolute is

$$[a(a + x)]^{2/3} - (by)^{2/3} = (a^2 + b^2)^{2/3}.$$

In order to determine the values of a and b for the hyperbola an outline of the plate was projected upon coördinate paper and corresponding values of x and y for a number of points were recorded. The best values for the a and b corresponding to the geometrical shadow were then found

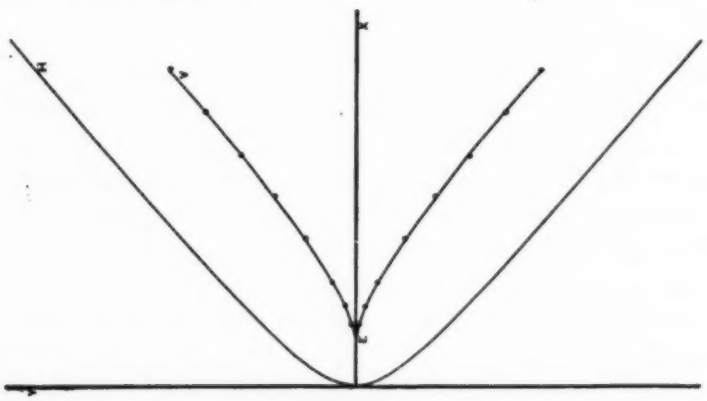


Fig. 1.

by the method of least squares to be 1.26 cm. and 1.08 cm. respectively. These values show upon computation that the hyperbola and its evolute do not intersect. The photograph indicates, also, that the same is true of the diffraction figure and the outline of the shadow.

Fig. 1 shows the hyperbola and corresponding evolute computed for the geometrical shadow using the values of a and b above. The circles indicate points taken at random from the diffraction curve on the photographic plate (Plate I., No. 1).

Fig. 2 illustrates similar curves for the parabolic shadow. The equation of the evolute for the parabola $y^2 = 4ax$, is

$$y^2 = 4(x - 2a)^3/27a.$$

These curves always intersect at the point $x = 8a$, $y = 4a\sqrt{2}$. This is in agreement with the photograph (Plate I., No. 2.)

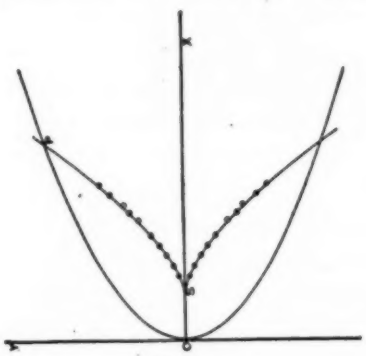


Fig. 2.

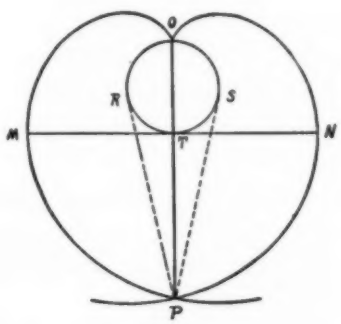


Fig. 3.

In order to apply this general principle of the diffraction evolute to other figures than conic sections a plate was cut in the form of the heart-shaped portion of the involute of a circle. This was done by unwinding a waxed thread from a small cylinder. A needle fastened to the free end of the thread was used to cut the outline of Fig. 3 from a sheet of heavy lead foil. From the construction it follows that the evolute of this curve is the original circle. Plate I., No. 3, reproduces the shadow of one of these heart-shaped plates and the diffraction figure accompanying it. The plate was about 2.5 cm. in length between the points of the heart, and was produced from a cylinder 8 mm. in diameter. The diameter of the circle as measured from the photograph agrees with that of the predicted evolute within 2 per cent.

It may be instructive to point out that there is not a one-to-one correspondence between the points of the circular evolute and those of the heart-shaped outline shown in Fig. 3. However, such correspondence does hold between the circle and the outline *MON*. This has been observed by placing a straight-edged screen over the portion *MPN* of the diffracting plate. In this case the whole circle was clearly visible. When the portion of the plate lying above *MTN* was covered the diffraction figure was only the arc *RTS*.

Examination of the photographic illustrations in this and in our preceding paper show that the shadows are crossed by a multitude of bright lines running normal to the edge. These lines are clearly developed in Plate I., No. 4, which was produced by a heart-shaped plate cut from paper, and the diffraction figure is seen to be a true envelope or caustic. From this it is probable that shadows and the diffraction patterns lying therein may be ascribed to the diffraction normals at the boundary of the shadow.

It seems, then, to be true in general *that whenever an object illuminated by a point source produces a diffraction pattern within its shadow, the predominant diffraction figure is the evolute of the geometrical shadow.*

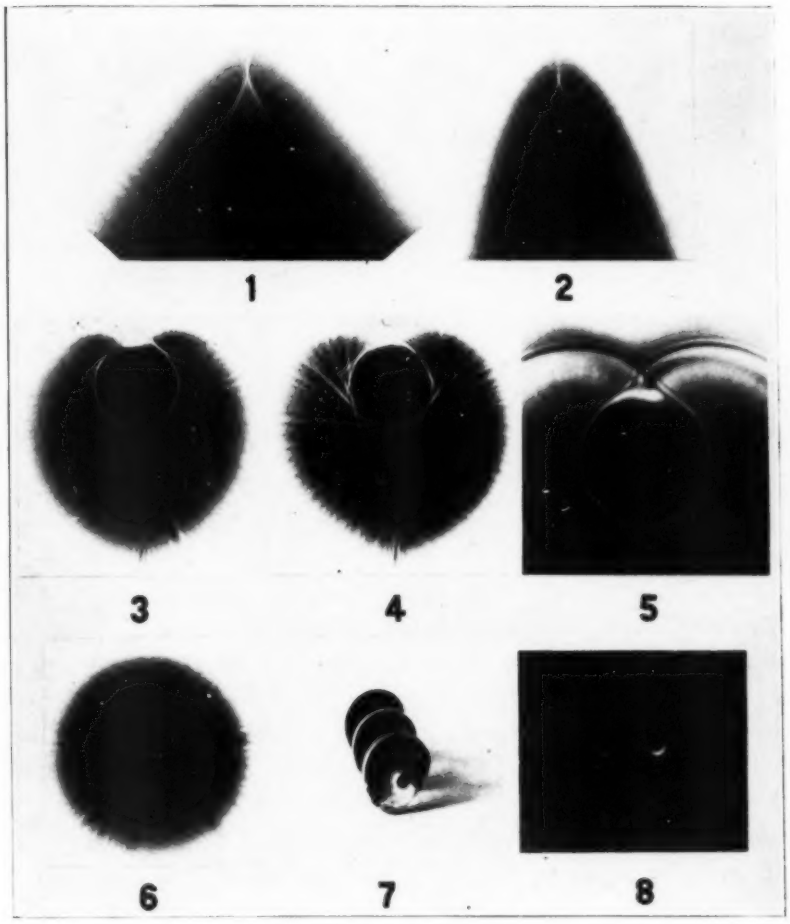
The production of the Arago spot has always been associated with the disc or sphere as the diffracting object. However, it was shown in our first paper on this subject that an elliptical plate producing a circular shadow also has associated with it a true Arago spot. A still more striking case is furnished by a diffracting object in the form of a spiral. Plate I., No. 6, is the circular shadow and Arago spot produced by a ¾-in. (1.90 cm.) auger bit of 1-in. (2.54 cm.) pitch ground to the form of a truncated cone and illuminated by a point source at the apex of the cone (see Plate I., No. 7).

If the axis of the cone is not accurately perpendicular to the wave front the shadow cast is not strictly circular, although it may apparently be so. In such a case the diffraction figure consists of two caustics. These are illustrated in No. 8. When the cone was reversed so that the apex was turned away from the point source, no adjustment whatever was capable of producing a true Arago spot. The nearest approach to a circular spot was crescent shaped with a dark shadow on the concave side, similar to one of the caustics in No. 8. It should be observed in this instance that the geometrical shadow could never be circular. The explanation of an Arago spot produced by such a device as the one here discussed, that is, by means of a spiral object, is a decided departure from the concept of Fresnel zones.

It may be said that the experiments discussed here and in the preceding paper seem to indicate the following general principle: *Any particular form of geometrical shadow is always associated with the same diffraction pattern whatever be the diffracting object.*

THE DETAIL IN THE STRUCTURE OF THE EVOLUTES.

It seems desirable to call attention to certain peculiarities of the diffraction evolutes of the conic sections. In order to make a more minute study of the formation of the evolutes of ellipses and circles the



G. G. BECKNELL AND JOHN COULSON.

distance from pinhole to photographic plate was increased from the usual distance of 7 meters to 20 meters. The diffracting plate was placed 3 meters from the pinhole instead of 2 meters. This arrangement produced about double the magnification previously used.

Plate II., No. 9, shows the diffraction pattern due to an ellipse of major diameter 1.6 cm. when placed with its plane perpendicular to the wave-normal. It will be observed that a series of bands lies *inside* the evolute and parallel thereto; and that the intensity of the bright bands diminishes rapidly as they recede from the evolute. The evolute consists of a number of separate flame-like streaks or "flares" which are merely the terminals of the bright bands within. As the eccentricity of the elliptic shadow diminishes the number of flares in a quadrant of the evolute decreases; and, therefore, likewise the number of bands within the evolute. This is illustrated by No. 10, taken for the ellipse above rotated through an angle of 25°. A similar decrease in the number of bands accompanies a reduction in the size of the plate when distances are kept constant.

A disc casting an elliptical shadow produces diffraction patterns identical with those just described when the dimensions of the shadows correspond. Plate II., Nos. 11, 12 and 13, were made with a disc .98 cm. in diameter, and correspond to angles of rotation from the normal position of 30°, 60° and 75° respectively. These illustrations bring out still more clearly the discontinuous nature of the diffraction evolute.

In the case of elliptical shadows there is always a set of bright and dark bands lying in the direction of the major axis. These become more distinct with increasing eccentricity of the shadow, as shown by Nos. 12 and 13. Similar strong bands appear in the patterns produced by an ellipse. When such a plate is rotated about its minor axis toward the position producing a circular shadow these bands gradually vanish, reappearing upon further rotation of the plate, but with an orientation in direction of 90°. That is, the direction of these bands in all cases is that of the *major axis* of the elliptical shadow.

Nos. 14, 15, 16 and 17, were taken with a carefully turned disc 5 mm. in diameter, the distance from source to photographic plate being increased to 33 meters. No. 14 shows the Arago spot and accompanying rings. Precisely the same pattern has been produced by an elliptical plate when casting a circular shadow. When the disc is rotated 20° from this position about an axis in its own plane No. 15 is produced. For angles up to 10° the transition in the pattern is almost imperceptible, but becomes more rapid beyond a rotation of 20°.

No. 16 corresponds to an angle of 30°. Here the bright spot

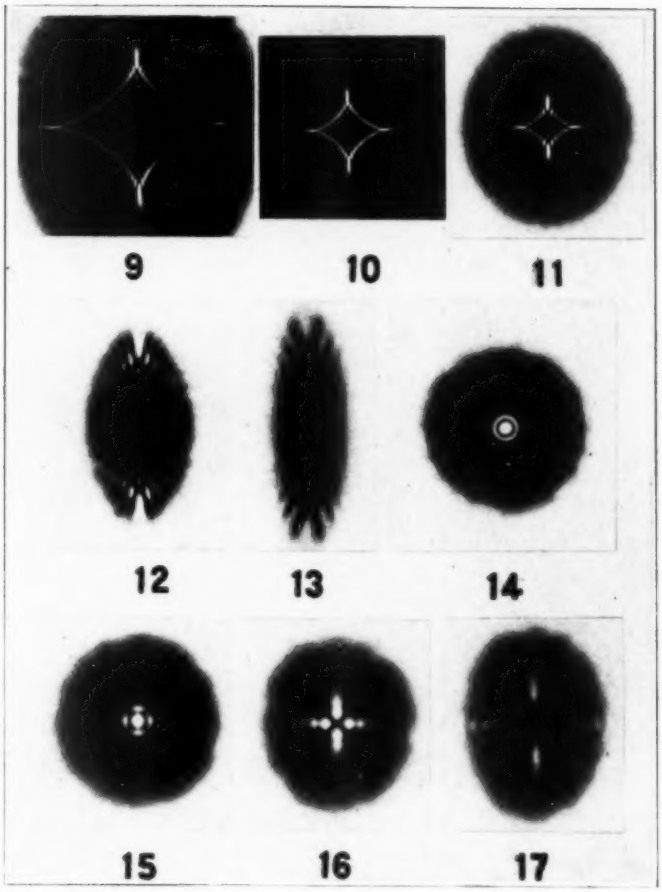
at the center has entirely disappeared and is replaced by a black figure resembling a pair of crossed dumb-bells with white knobs faintly appearing at the ends of the bars. These knobs become brighter upon further rotation of the disc. At approximately 45° a bright spot reappears at the center of the figure with a pattern as shown in No. 17. It will be observed in the last two figures that the rings which surrounded the original Arago spot have changed decidedly in shape. In No. 16 they appear elliptical while in No. 17 they are oval. The major diameter of each figure is along the minor axis of the elliptical shadow.

Very definite transitions in color were observed as the disc was rotated beyond the position represented by No. 15. The central spot remains white up to about 22.5°, shading into pink with increasing angle and becoming distinctly red at 27.5°. At 30° the spot has entirely disappeared. On further rotation of the disc a central spot gradually reappears, showing green at 35°, surrounded by four white spots in the form of an upright cross as in No. 16. Four distinctly red knobs appear on the crossed dumb-bells in this figure. At 45° the central dot changes to red, closely surrounded by four streaks of green, as in No. 17. At 50° the center again is black, and the four streaks have changed to white. The four flares on the axes always remain white.

Attention has been called to the fact that in the case of elliptical shadows a set of "secondary" bands lie *inside* the evolute and parallel to it, while another set extend along the major axis. The hyperbola and parabola, also, give rise to a similar series of bands. However, in Plate I., No. 3, the secondary bands occur on the *outside* of the circular evolute, and none on the inside which appears to be absolutely dark. The latter point is explained by the fact that the circular area is not traversed by any of the diffraction normals from the edge of the shadow. No. 5 shows that these secondary bands intersect at the cusp of the heart and become continuous with the usual diffraction bands lying outside the shadow.

In the case of all shadows in the form of conic sections the evolute is the envelope of the normals to the edge of the shadow which emanate from the opposite side of the axis. Thus, the areas outside the evolute are traversed by only one set of these normals; and, therefore, the secondary bands cannot exist within these areas.

UNIVERSITY OF PITTSBURGH,
July, 1922.



G. G. BECKNELL AND JOHN COULSON.

NEW EVIDENCE REGARDING THE INTERPRETATION OF CRITICAL POTENTIALS IN HYDROGEN.

BY P. S. OLMSTEAD.

SYNOPSIS.

Critical Potentials in Hydrogen.—(1) *Experimental separation of effects due to atomic and molecular hydrogen.* In an ionization tube of the Lenard type, a close grid of tungsten wires was introduced between the filament and the gauze in front of the plate. When this grid was heated electrically to incandescence the proportion of atoms was greatly increased by dissociation of the molecules. (2) *Effects due to radiation were distinguished from effects of ionization* by comparing the electron currents to a disk electrode with those to a wire which because of its small area was relatively insensitive to effects of radiation. (3) *Six critical potentials between 10 and 16 volts* were observed and measured with reference to the strongest break, assumed to occur at 16.0 volts. Each break point was located at the intersection of two tangents; hence the relative values are probably accurate to 2 or 3 per cent. Purified electrolytic hydrogen was used. (4) *Experimental interpretation* of the breaks, which agrees in general with the previous theoretical interpretation based on quantum theory, is as follows: radiation from the atom at 10.1 and at 12.2 volts, corresponding to the first two terms of the Lyman series; ionization of the molecule at 11.5 volts and of the atom at 13.6 volts; dissociation of the molecule and radiation at 12.9 volts; finally, dissociation of the molecule and ionization of one of its parts at 16.0 volts. The energy required for dissociation of the molecule is therefore equivalent to about 2.8 volts.

INTRODUCTORY.

THE conclusions, which have been published by recent investigators on the critical potentials of hydrogen, were collected and tabulated in a recent paper by Professor K. T. Compton and the author.[1] Since that time, reports by Mohler, Foote, and Kurth[2] and O. S. Duffendack[3] and a paper by P. E. Boucher[4] have been added to the list of references. The effects which have been observed fall under five heads, which are noted in Table I.

TABLE I.

Type of Effect.	Due to	First Observed at
Radiation	Atom	10.0 to 11.0 volts
Ionization	Molecule	10.8 to 11.5 volts
Dissociation plus radiation	Molecule	12.5 to 13.9 volts
Ionization	Atom	13.1 to 14.4 volts
Dissociation plus ionization	Molecule	15.8 to 17.1 volts

[1] K. T. Compton and P. S. Olmstead, PHYS. REV., 17, 45, 1921.

[2] Mohler, Foote and Kurth, PHYS. REV., 19, 414, 1922.

[3] O. S. Duffendack, PHYS. REV., 19, 533, 1922.

[4] P. E. Boucher, PHYS. REV., 19, 189, 1922.

Except in the work of Mohler, Foote, and Kurth and of Duffendack, the interpretations which appear in the second column of the table are the result of comparison of observed radiation and ionization potentials with the theoretical potentials based on some theory of the hydrogen molecule. The present paper deals with an *experimental separation* of the effects which are due to the atom from those which are due to the molecule.

APPARATUS. TREATING OF ITS SPECIAL FEATURES.

The apparatus used in this work was the one which was described in a previous paper[1] as one to "permit of more refined observations to test some of the considerations involved in the problem." In Fig. 1 it is

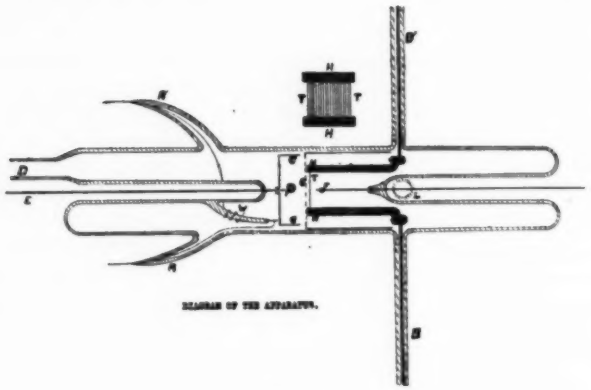


Fig. 1.

seen in cross-section. It consisted of a glass tube containing the usual elements of a Lenard typ of ionization tube, with the addition of a heating arrangement placed as close as possible to the gauze. At *F* was a spiral tungsten filament (seen in cross-section, end on), across which the voltage drop was 1.6 to 1.7 volts for a current of 3.5 to 4.0 amperes. The spiral consisted of three turns only, in the middle of the filament. Since this part of the filament was hotter than the rest, and since the potential drop across the spiral part was but a small fraction of a volt, the filament was practically an equipotential source of electrons. At *G* was a gauze covering one end of a platinum cylinder, which was connected with the galvanometer by a lead through a side-tube *L*, in order to measure the total electron emission from the filament. As close as possible to the gauze and between it and the filament, was a heating grid, consisting of twenty fine tungsten wires *TT* strung between two copper plates *HH* so that the wires of the grid were perpendicular to the filament.

[1] Loc. cit.

The copper plates were insulated from the gauze and its supporting cylinder by small quartz blocks. The electrical connections to the grid were made by means of heavy copper wires to the plates sealed through the long glass tubes BB^1 with De Khotinsky cement at their ends. It was necessary to keep these tubes very cool to prevent the cement from melting due to the heat conducted along the wires. The second special feature of the apparatus was the receiving electrode or plate. This consisted of two parts—a single platinum wire P of small cross-sectional area, and a platinum cup C which surrounded P and could either be joined to P or insulated from it. When joined and connected to the electrometer the combined effect of radiation and ionization was observed, while if P alone were connected to the electrometer, ionization only was measured, since the area of P was too small to intercept enough radiation to give an appreciable photoelectric effect. Suitable guard rings were placed at strategic points to prevent leakage to the electrometer. One of these is shown at W. At D was a connection to the diffusion pump, McLeod gauge, and source of hydrogen. Between them and the tube were two liquid air traps, the one nearest the tube being filled with coconut charcoal.

The hydrogen was obtained as in the previous work by the electrolysis of sulphuric acid. The processes involved in purifying the gas are explained in the previous paper. The tube was "baked out" by heating in a furnace to about 300° C., keeping the tube pumped out at the same time. It was further cleansed of the unwelcome residual gas by "washing out" with hydrogen, the hydrogen being introduced and pumped out at various times during the baking.

The tungsten grid TT, placed as close to the region of effective electron impacts as possible without introducing disturbing effects from positive thermions, served to vary the proportion of dissociated, or atomic, hydrogen.[1] Any effect which was relatively enhanced by raising the grid to a high temperature must be due to atomic hydrogen. Similarly, any effect which was relatively more pronounced when detected by the point P than by the cup C was attributed to ionization.

The method of obtaining the experimental readings was such as to give the greatest relative accuracy. Under the same conditions of gas pressure and current flow in the gas, as observed in the galvanometer deflections, it was possible to duplicate the values of the electrometer readings at specified accelerating voltages to within two or three per cent. in different runs, even in the region of greatest variation of the electrometer readings with the accelerating voltage, *i.e.*, in the region from

[1] Langmuir, Jour. Amer. Chem. Soc., 37, 417, 1915.

15 to 16 volts. In fact the individual curves from which the "Grid off for Radiation" average curve (Fig. 2) was obtained differed from the average by less than one per cent.

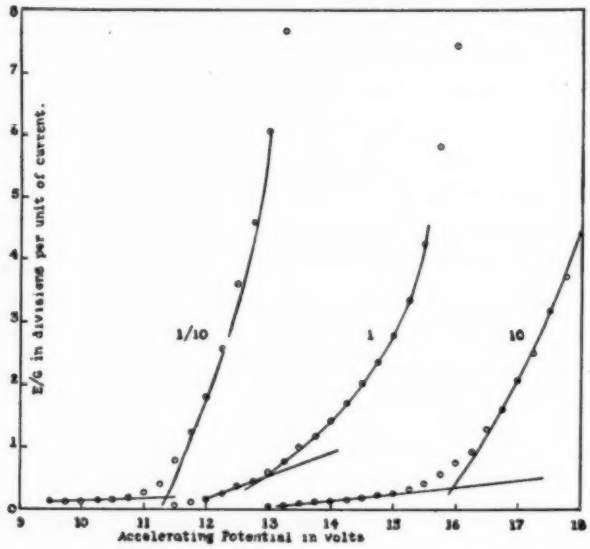


Fig. 2.

"Grid off for Radiation" Curve Breaks: 11.4; 12.9; 16.0.

EXPERIMENTAL RESULTS.

In this tube are two totally independent elements which may be varied independently, and hence we expect to find four types of experimental results. First, we may connect only the platinum point P to the electrometer, and have the grid on. Curves obtained with this set-up are called "Grid on for Ionization" curves and will be denoted by I (on). Next, we may keep the electrometer connections the same but turn the grid off. This gives a set of "Grid off for Ionization" curves and they will be denoted by I (off). The two other possibilities are obtained by connecting the cup C as well as the point P to the electrometer, giving the arrangement suitable for observing the combined effect of radiation and ionization. We then get the sets of curves—"Grid on for Radiation," R (on), and "Grid off for Radiation," R (off). These four types of curves are illustrated by the average curves (Figs. 2, 3, 4 and 5), each of which is the average of a number of independent runs. These curves have been corrected from the observed relations by adjusting the accelerating voltage on each of the original curves so that the big "break," which corresponds to dissociation of the molecule plus ionization of one

of its parts, may come at 16.0 volts. The adjustment was an empirical one which made the line representing the slope of the curve after passing the break point cut the line representing the slope of the curve before reaching the break point. Since this intersection depends largely on the

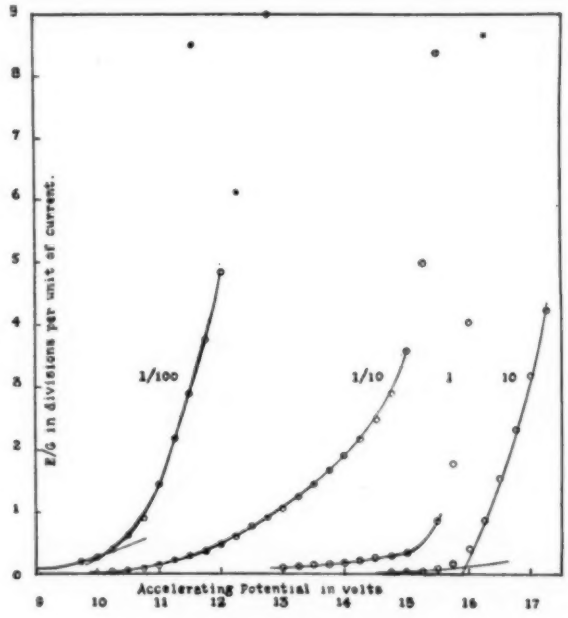


Fig. 3.

"Grid off for Ionization" Curve Breaks: 10.1; 11.5; 16.0.

way in which the intersecting lines are chosen, the plots were consistently made so that the line on either side of the break point was fairly straight for a region of two volts. Velocity distribution curves were not generally taken, since the object of this work was to find the peculiarities of the lower breaks and to locate their positions relative to the large breaks.

In order to obtain a convenient comparison between the different effects, four ratio curves were computed. These are based on the four average curves typifying the four sets of experimental results. Each of these average curves shows the average of several experimental curves which were taken under approximately similar conditions of pressure of hydrogen, and, to a certain extent, of electron current as given by the galvanometer readings. With regard to this it was found that, if the pressure and accelerating voltage were kept constant, the ratio of the electrometer reading to the galvanometer reading E/G would be approximately constant. Thus in all these results it is this ratio, or the electrometer deflection per unit bombarding current of electrons, which

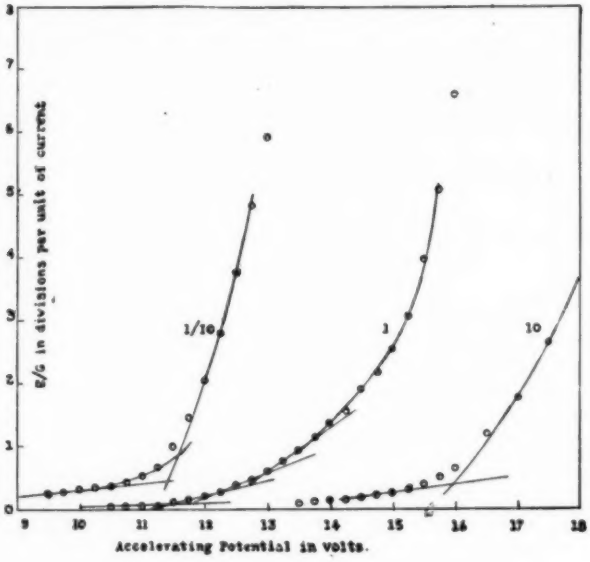


Fig. 4.

"Grid on for Radiation" Curve Breaks: 10.2; 11.4; 12.2; 12.9; 13.7; 16.0.

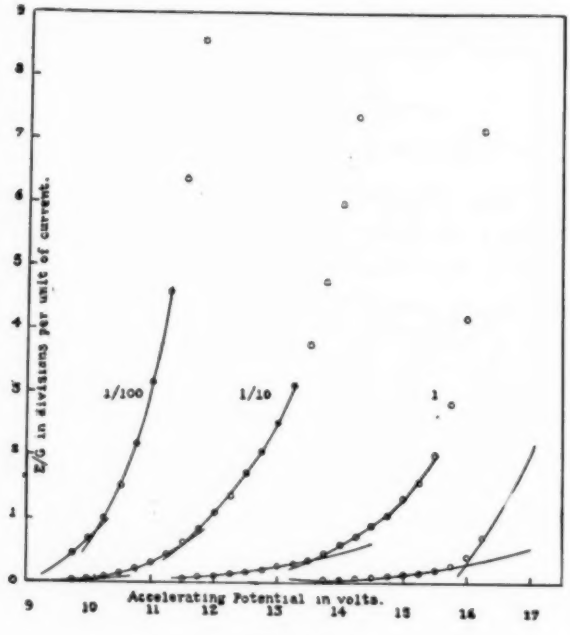


Fig. 5.

"Grid on for Ionization" Curve Breaks: 10.1; 11.5; 13.6; 16.0.

has been plotted against the accelerating voltage. Then from these curves were obtained the ratio curves:

$$\frac{I\ (\text{on})}{I\ (\text{off})}, \quad \frac{R\ (\text{on})}{R\ (\text{off})}, \quad \frac{R\ (\text{on})}{I\ (\text{on})}, \quad \frac{R\ (\text{off})}{I\ (\text{off})}.$$

These are shown in Figs. 6, 7, 8 and 9. The values for the points for

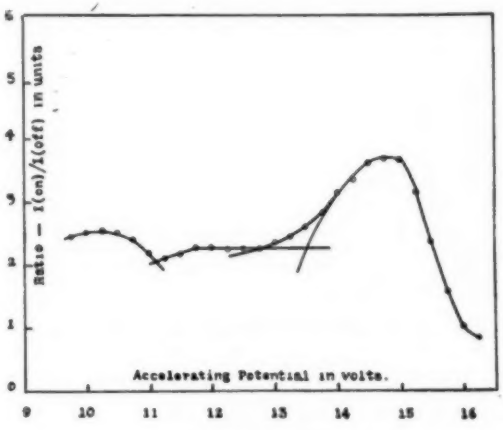


Fig. 6.

Ratio Curve for I (on)/I (off).

these ratio curves were obtained from the calculated values of the averages rather than by reading the curves, so that the ratio curves themselves are experimental curves and have not been smoothed by smoothing the average curves in any way.

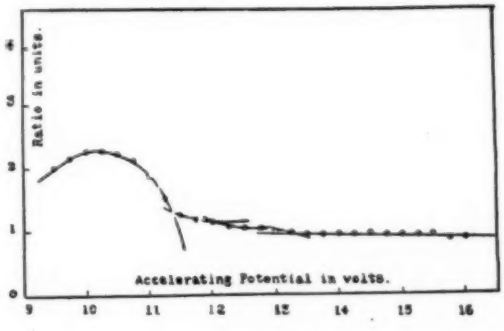


Fig. 7.

Ratio Curve for R (on)/R (off).

DISCUSSION OF RESULTS.

The interpretation of these results will be considerably facilitated if first a careful study is made of the way in which the individual ratio curves

should behave. Take, for instance, the ratio I (on)/I (off), Fig. 6. With the grid on we should get a greater concentration of atomic hydrogen; hence when this ratio is greater than unity it means that the effect due to the atom has been increased relative to that due to the molecule. Thus, any effect which tends to bend the ratio curve toward the unity

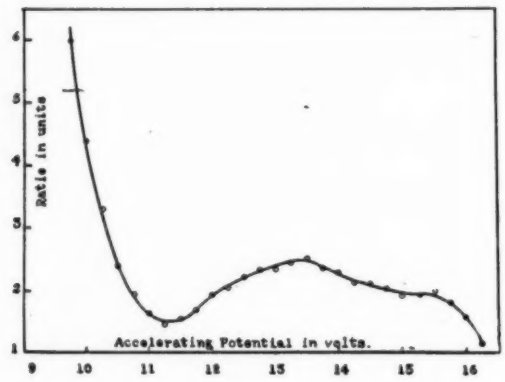


Fig. 8.

Ratio Curve for R (on)/I (on).

line would be interpreted as an increase in an effect due to the molecule while anything which turns the slope away from the unity line would be taken as due to the atom. The same thing may be said of the ratio R (on)/R (off), Fig. 7. Now let us consider the conclusions which may be drawn

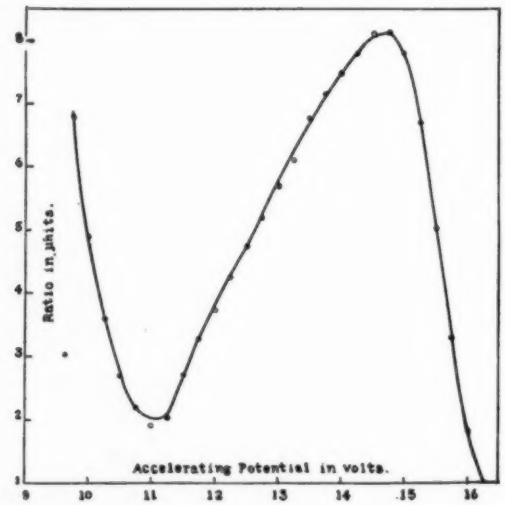


Fig. 9.

Ratio Curve for R (off)/I (off).

from the two curves. If the ionization curves should show the increased effect due to the hot grid, but the radiation curves should not, the effect itself would be taken as ionization and also as due to the atom. In like manner it is possible to get further differentiations of ionization and radiation.

TABLE II.

Data Obtained from the Ratio Curves.

Range of the Effect (Volts).	Interpretation.	Reason.
9.50 to 10.2...	Radiation from atom	$\frac{R\ (\text{on})}{I\ (\text{on})}$ and $\frac{R\ (\text{off})}{I\ (\text{off})}$ both start high.
		$\frac{R\ (\text{on})}{R\ (\text{off})}$ curve starts high and increases.
10.2 to 11.4....	Ionization due to molecule	Both $\frac{R}{I}$ curves decrease sharply.
		Effect is not increased by grid on.
11.4 to 12.1....	Radiation from atom	Strong increase in $\frac{R}{I}$ curves.
		Upward tendency in $\frac{R\ (\text{on})}{R\ (\text{off})}$ curve.
12.1 to 13.0....	Radiation from molecule	$\frac{R}{I}$ curves show no falling off.
		$\frac{R\ (\text{on})}{R\ (\text{off})}$ curve slightly deflected downward.
13.0 to 15.0....	Ionization due to atom	$\frac{R\ (\text{on})}{I\ (\text{on})}$ curve strongly flattened.
		$\frac{R\ (\text{off})}{I\ (\text{off})}$ curve practically unaffected.
		$\frac{I\ (\text{on})}{I\ (\text{off})}$ curve increases strongly.
		$\frac{R\ (\text{on})}{R\ (\text{off})}$ curve very slightly inflected upward.
15.0 to limit of investigation.	Ionization due to molecule	Strong decrease in $\frac{R}{I}$ curves.
		No increase in $\frac{R\ (\text{on})}{R\ (\text{off})}$ curve.
		Strong decrease in $\frac{I\ (\text{on})}{I\ (\text{off})}$ curve.

The other two ratio curves also have certain peculiarities. The grid remains unchanged while the type of effect is varied. If the radiation effect is large relative to the ionization effect, the curve will be greater than unity, whereas if the effect is mainly ionization the curve will tend

to remain near unity. Those effects which tend to bend the curve away from the unity line are due to radiation and those which tend to bend it toward the unity line are due to ionization.

Considered with this interpretation of their behavior, these four curves make it possible to construct Table II. This shows the whole field of the investigation blocked off into units, and gives the type of effect that is most important in each unit. It remains to indicate the way in which these units are consistent with the breaks that appear on the experimental curves (Figs. 2, 3, 4 and 5). As in the case of the ratio curves we will first consider what may be expected to happen in each of these average curves. With the grid off we should not expect effects due to the atoms, but on the other hand effects due to molecules would be very sharp. Thus on the "Grid off for Ionization" curve only ionization from molecules should be observed. Similarly, on the "Grid off for Radiation" curve we should observe radiation and ionization from the molecules only. On the other hand the curves with the grid on should give both the molecular and atomic effects. The "Grid on for Radiation" curve should give all the breaks and the "Grid on for Ionization" curve all the ionization but none of the radiation effects. Accordingly, if we turn to the curves themselves, we may classify our results as shown in Table III. We note that, except for the last item, just the effects expected according to the above analysis are observed. We are therefore compelled to ask the question, "Why do we get an effect due to radiation

TABLE III.

Breaks Observed on the Experimental Curves.

Position.	Observed at (Volts)	Interpretation.	Curve.
16.0.....	16.0	Dissociation of molecule plus ionization of one atom	"Grid on for Ionization"
	16.0		"Grid off for Ionization"
	16.0		"Grid on for Radiation"
	16.0		"Grid off for Radiation"
13.6.....	13.6	Ionization of atom	"Grid on for Ionization"
	13.7		"Grid on for Radiation"
12.9.....	12.9	Dissociation of molecule plus radiation from one atom	"Grid on for Radiation"
	12.9		"Grid off for Radiation"
12.2.....	12.2	Radiation from atom	"Grid on for Radiation"
11.5.....	11.5	Ionization of molecule	"Grid on for Ionization"
	11.5		"Grid off for Ionization"
	11.4		"Grid on for Radiation"
	11.4		"Grid off for Radiation"
10.1.....	10.1	Radiation from atom	"Grid on for Ionization"
	10.1		"Grid off for Ionization"
	10.2		"Grid on for Radiation"

from the atom in three sets of curves when we expect it only in one?" This is easily answered when the electrical connections which were used for ionization and for radiation are considered. It is seen that in the "Grid off for Radiation" curve the effect is not observed, which is as expected. With the connections for ionization, however, there is a larger volume of gas in which the effective collisions take place and, since no ionization of any kind was detected below 11.5 volts, any small effect before that must be due to radiation. To account for a certain amount of atomic effect present even when the grid is off we turn to the filament itself. This is very hot, and besides giving off electrons, is able to decompose a certain amount of the gas near it. Whatever effect is present in the region of 10 to 11 volts would be more noticeable than any effect of the same order of magnitude farther up in the curve where it would be superimposed on another effect of a much larger magnitude. For this reason it is possible to detect the radiation from the 10.1 volt effect even with the point P alone as the detecting electrode.

In discussing these curves we should not overlook the characteristics of the breaks. We note that the break at 16.0 volts is not as sharp nor as distinct as the others but seems to start a volt or more before the steep rise in the curve takes place. We note that the other breaks are singularly distinct, so that it is usually possible to draw smooth curves on either side of the break so that they either pass through all the observed points or at most neglect one or two. The obvious explanation of this difference is that it is due to the fact that all the electrons emitted by the filament do not have the same velocity, so that it is possible for some of the electrons to have the velocity required to produce the observed effect with a smaller accelerating potential than others. For this reason we need a sliding scale to determine at what true voltage the various effects set in.

Suppose that P_m is the probability of an electron striking a molecule of gas; P_a the probability of striking an atom of the gas; and p the probability of an electron being emitted from the filament with a velocity sufficient to produce the desired effect. P_m will be proportional to the number of molecules in a unit volume of the gas and therefore is practically proportional to its pressure, since the partial pressure of the atoms is always small. In like manner the value of P_a will be proportional to the number of atoms in the gas. We know that there is always a relationship between the number of atoms and molecules which remain in equilibrium at any temperature. This relationship depends on thermodynamical considerations. If we supply energy to the gas we can keep a larger proportion of the particles in the atomic form. In this work

this was made possible by the introduction of the heating grid. Even when the grid is off a certain amount of atomic hydrogen will be in the tube due to dissociation by the filament itself. This, of course, is not formed at the place where it is most effective and thus it will be observed only when the other effects are almost negligible in comparison. To take a numerical analogy to the situation here, suppose that there were in the case with the grid off 99 molecules to every 1 atom. Then the observed effects due to the molecule would be 99 times as strong as that due to the atom. Then let us suppose that with the grid on we have 90 molecules to every 10 atoms. Now the effect due to the molecule is only 9 times that due to the atom, but we have also changed two other factors. The effect due to the atom has been increased 10 times and the effect due to the molecule has been slightly decreased, but has practically the same value as before. Thus we see we can express the probability of striking an atom in terms of the probability of striking a molecule as

$$P_a = kP_m,$$

where k is a constant depending on the linear relation of the number of atoms to the number of molecules, or in this particular case on the amount of dissociation produced by the grid. But, in addition to striking a molecule or atom, we must have a transfer of energy at the collision in order to produce the desired effect. If the electron making the collision does not have sufficient energy to produce the effect, the energy cannot be transferred. On the other hand, if the electron has more, it can, of course, give it. We know that the energy of an electron is proportional to the square of its velocity, so if we assume Maxwell's Law of Distribution of Velocities we can get an idea of the probability of having a particular velocity or more, and in so doing get a corresponding probability of having a specified amount of energy or more. This is a more difficult thing to consider. In Table IV. is given, against tenths of the mean energy, the percentage of electrons having less than the specified part of the mean energy (F), the percentage of electrons having more than the specified part of the mean energy ($1 - F$), the percentage of electrons having energies in the interval between two successive specified divisions of the energies (dF), and the mean energy of all electrons having energy greater than the amount specified in the first column. This is expressed in terms of the mean energy of all the electrons and in equivalent volts. Thus, to take a specific example, 50.64 per cent. of the electrons have less than 0.8 times the mean energy, 49.36 per cent. have more, and the mean energy of these 49.36 per cent. is 1.61 times the mean energy of all the electrons, or 0.97 volt. The expression in equivalent volts is obtained from the

average correction for a filament temperature of 2350° to 2400° K. This has been found to be 0.60 volt.[1] The values given in the last two columns were obtained by mechanical integration, the steps used being those tabulated.

TABLE IV.

No. of Times Mean Energy.	F.	$1 - F$.	dF.	Mean Energy of Group $(1 - F)$.	
Times $\bar{E}$.	%	%	%	Times $\bar{E}$.	Volts.
0.0	0.00	100.00		1.00	0.60
0.1	3.99	96.01	3.99	1.04	0.62
0.2	10.35	89.65	6.36	1.10	0.66
0.3	17.46	82.54	7.11	1.18	0.71
0.4	24.70	75.30	7.24	1.26	0.76
0.5	31.77	68.23	7.07	1.34	0.81
0.6	38.51	61.49	6.74	1.43	0.86
0.7	44.81	55.19	6.30	1.52	0.91
0.8	50.64	49.36	5.83	1.61	0.97
0.9	55.97	44.03	5.33	1.70	1.02
1.0	60.84	39.16	4.87	1.79	1.07
1.1	65.24	34.76	4.40	1.89	1.13
1.2	69.22	30.78	3.98	1.98	1.19
1.3	72.75	27.25	3.53	2.08	1.25
1.4	75.93	24.07	3.18	2.18	1.31
1.5	78.77	21.23	2.84	2.27	1.36
1.6	81.30	18.70	2.53	2.37	1.42
1.7	83.54	16.46	2.24	2.46	1.48
1.8	85.53	14.47	1.99	2.56	1.54
1.9	87.28	12.72	1.75	2.66	1.60
2.0	88.84	11.16	1.56	2.76	1.66
2.2	91.42	8.58	2.58	2.96	1.78
2.4	93.48	6.52	2.06	3.18	1.91
2.6	94.96	5.04	1.48	3.41	2.05
2.8	96.16	3.84	1.20	3.63	2.18
3.0	97.07	2.93	.91	3.85	2.31
3.5	98.52	1.48	1.45	4.44	2.66
4.0	99.26	.74	.74	5.12	3.07
5.0	99.72	.28	.46	6.15	3.69
6.0	99.88	.12	.16	7.00	4.20

Applying this to the curves that we have obtained, we get the information given in Tables V. and VI. Here we have assumed that at the 16.0-

[1] Sih Ling Ting, Roy. Soc. Proc., 98, 374, 1921.

volt break we can express the magnitude of the new effect coming in as a function of the number of electrons with sufficient energy to produce the effect. If no new effect were coming in, the curve would continue to increase smoothly and, supposedly, would tend to flatten out, but the new effect starts the curve upward again. In the early part of the curve this effect is due only to a few of the electrons, but, with increasing voltage, more are able to produce the effect. It is assumed that in this interval of about a volt or a volt and a half the major part of the difference between the extrapolated curve and the observed curve is due to the distribution of velocities. To obtain a significant quantity the difference between the observed and extrapolated curves was divided by the percentage of electrons with total energy sufficient to take part in producing the effect. If we are correct in assuming that all electrons with energies greater than 16 volts are equally likely to produce ionization at impact (which is probably nearly true in the small range of velocities

TABLE V.

Accel. Poten., Volts.	Correction.		Per Cent. having this Correction.	Grid off for Radiation.				Grid on for Radiation.			
	Volts.	$\bar{E}$.		Reading.	Extr. Curve.	Difference.	Diff. %	Reading.	Extr. Curve.	Difference.	Diff. %
15.00	1.75	2.92	2.8	2.8	2.8	0.0	0.00	2.5	2.5	0	.00
15.25	1.50	2.50	4.5	3.3	3.2	0.1	0.02	3.1	2.9	0.2	.05
15.50	1.25	2.09	7.5	4.2	3.6	0.6	0.08	4.0	3.1	0.9	.12
15.75	1.00	1.67	12.7	5.8	4.0	1.8	0.14	5.1	3.4	1.7	.13
16.00	0.75	1.25	21.5	7.4	4.4	3.0	0.14	6.6	3.8	2.8	.13
16.25	0.50	0.84	37	9.2	4.8	4.4	0.12	8.6	4.1	4.5	.12
16.50	0.25	0.42	62	12.9	5.2	7.7	0.12	11.9	4.5	7.4	.12
16.75	0.00	0.00	100	16.1	5.6	10.5	0.11	14.5	4.8	9.7	.10

TABLE VI.

Accel. Poten. Volts.	Correction.		Per Cent. Having this Correct.	$(\%)^{3/2}$.	Grid off for Ionization.				Grid on for Ionization.			
	Volts.	$\bar{E}$.			Reading.	Extr. Curve.	Difference.	Diff. $(\%)^{3/2}$.	Read.	Extr. Curve.	Difference.	Diff. $(\%)^{3/2}$
15.00	1.75	2.92	2.8	4.7	0.4	0.4	0.0	0.000	1.3	1.3	0.0	0.000
15.25	1.50	2.50	4.5	9.6	0.5	0.4	0.1	0.010	1.6	1.4	0.2	0.022
15.50	1.25	2.09	7.5	20.6	0.9	0.4	0.5	0.024	2.0	1.6	0.4	0.019
15.75	1.00	1.67	12.7	45.6	1.8	0.4	1.4	0.031	2.8	1.8	1.0	0.022
16.00	0.75	1.25	21.5	100	4.1	0.5	3.6	0.036	4.2	2.0	2.2	0.022
16.25	0.50	0.84	37	227	8.7	0.5	8.2	0.036	7.1	2.1	5.0	0.022
16.50	0.25	0.42	62	490	15.2	0.5	14.7	0.030	—	—	—	—
16.75	0.00	0.00	100	1,000	23.2	0.6	22.6	0.023	—	—	—	—

considered) then this ratio should be constant. For the radiation curves as given in Table V. we see that the constancy of the ratio is well established from 15.75 to 16.50, a region about one volt in length. This is about as much as can be expected. In these calculations, though provision is made for the increasing effect of the new break, we have not made the further correction in the falling off of the old break. If this is done Tables V. and VI. are changed to Table VII. In Table VI. we

TABLE VII.

Accel. Poten. Volts.	R (off) $\frac{Diff.}{\%}$	R (on) $\frac{Diff.}{\%}$	I (off) $\frac{Diff.}{(\%)^{3/2}}$	I (on) $\frac{Diff.}{(\%)^{3/2}}$
15.00	0.03	0.03	0.000	0.000
15.25	0.07	0.07	0.010	0.031
15.50	0.12	0.15	0.024	0.029
15.75	0.18	0.17	0.033	0.026
16.00	0.18	0.17	0.038	0.026
16.25	0.17	0.16	0.037	0.026
16.50	0.18	0.16	0.031	——
16.75	0.16	0.15	0.023	——

note that in order to obtain even an approximation to linearity the three-halves power of the per cent. must be used. This only goes to show that conditions in the tube are different in the two types of effect. It may well be that when a charged nucleus is accelerated only in the direction of emission of the electrons the effects due to it are linear but when it is forced to move in a curved path it obeys a different law. This is the case in the present problem. When the connections are arranged for observing radiation and ionization together, the charged molecules or atoms move on toward the plate in straight lines. On the other hand, in the arrangement to observe only ionization these particles are accelerated in a direction different from that in which they were moving. For this reason they will be traveling in orbits which will approximate parabolas with the wire point as their foci. Only in the case when the attraction is sufficiently great to bring the orbit within the small region occupied by the wire will the effect of the charged particle in the orbit be recorded. Another factor tending to increase the effect in the ionization curves is that more molecules and atoms may participate in collisions which will give observable effects. This is illustrated in Figs. 10 and 11. In Fig. 10, all the collisions must take place in the neighborhood of the gauze while in Fig. 11, the collisions may take place in the whole region surrounded by the gauze and cup which are kept at the same potential. We find by a study of the results that the effect is increased so that it varies with the three-halves power of the accelerating voltage.

Up to this point the question of the determination of the position of the break point has been based on an arbitrary assumption that the curve assumes a more or less linear character both before and after the break point. Nothing has been mentioned to indicate whether this type

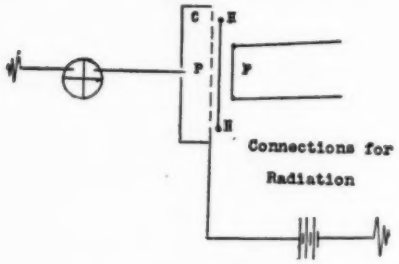


Fig. 10.

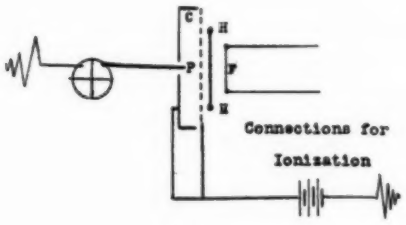


Fig. 11.

of determination of the break should be more or less accurate than the usual one of taking the point of rise in the curve as the real break point. It has just been shown, however, that the curve has a roundness at the break point providing the break is so pronounced that the effect of the distribution of velocities becomes an important factor. If we consider the weaker breaks, which do not have this large distribution of velocity factor, we find that the curve on the two sides of the break is almost given by straight lines which are inclined to each other at a small angle. This means that if we were able to obtain a more accurate set of values near this point and could plot them on a larger scale we would find a similar distribution of velocity curve. Conversely, if we should plot on a much smaller scale the curve near the stronger breaks, where we observe the distribution of velocity correction, we would find that the limit of the curve would be two straight lines intersecting at the break point. This is the real significance of this criterion for a break. It actually makes the position of the break independent of whether the effect observed is large or small. Now concerning the accuracy with which the break is fixed, we must again consider these two types of effect. The large effects are sometimes so large that the scale must change at least once in passing through the break point. This means that we must use care in selecting the particular curve which gives the correct break point. Obviously the only one to use is the one to a scale which can show the curve for at least one or two volts on either side of the break point. The intersection of the tangents which most nearly express the remaining portion of the curve on either side of the break then gives the correct break point. We find that this gives a probable error of about .2 volt in almost every case. Thus we obtain all breaks properly spaced

relatively to each other, independent of the velocity distribution, if we determine the position of each when plotted to a scale giving a difference of slope on each side of the break which is the same for all.

We must also try to determine the absolute accuracies of the points of discontinuity of each curve. Turning to the spectroscopic evidence we note that the 10.1-volt and the 13.5-volt breaks can be accurately computed while the breaks which are due to the molecule do not have this additional check. We have already shown that the accuracy of the big break is $\pm$ .2 volt, so we can easily compare the points at which the breaks occur and then discuss the accuracy of the positions. If we compare the values for the small breaks with the values predicted on the Bohr Theory and find how they are fixed relative to each other we find that the agreement is extremely good. So we are left with only one break to fix and we have one bit of evidence that helps us to fix that relatively to the others. Among the small breaks is the one for "dissociation of the molecule plus radiation from an atom." This was found to be 2.8 volts higher than "radiation from the atom." This 2.8 volts is therefore the energy required for dissociation of the molecule. That means that in order to fix the value for "dissociation of the molecule plus ionization from one atom" we must have from the figures which are given 13.6 + 2.8 or 16.4 volts. The result obtained was 16.0 $\pm$ .2 volts so that the values check with a maximum accuracy of .2 volt, or to a minimum accuracy of .6 volt. The most probable tendency is to place the big break too soon, for the observer is always anxious to note the beginning of an effect though it might be better for him to determine the point at which the full effect comes in rather than any intermediate point. In this case we might suppose that the small breaks were observed only when the velocity of all electrons was sufficient to give the observed effect. This would correspond, in the case of the big break, to the point at which the intermediate curve had a slope corresponding to the slope of the curve beyond the break. This adds about .5 volt to the previous observed value, giving us 16.5 as a better position of the break. This seems to agree a bit better with the other calculation. However, these suggestions are such as to show that the results are in good agreement and are really not sufficient to definitely settle the exact position of the big break. Probably this last correction, which brings the value up to 16.5 volts, is in reality too much and the actual position is somewhere between 16.0 and 16.5 volts. This seems the only logical conclusion at which we can safely arrive.

CONCLUSION.

As a result of this research, Bohr's Theory of the Hydrogen Atom has been experimentally closely verified, since both the first and second radiation potentials, corresponding to the first two terms of the Lyman Series, have been obtained. In addition it has been conclusively shown that two ionizing potentials of the molecule exist, the first at 11.5 volts leaving the molecule positively charged, while the second at 16.0–16.5 volts dissociates the molecule and ionizes one of its parts.

In conclusion, the writer wishes to express his sincere thanks to Professor K. T. Compton for his suggestions and assistance in carrying out the investigation.

PALMER PHYSICAL LABORATORY,
PRINCETON UNIVERSITY,
June, 1922.

Note: Fig. 10 should show the point P and the cup C electrically connected and insulated from the gauze.

POSITIVE-RAY ANALYSIS OF POTASSIUM, CALCIUM AND ZINC.

By A. J. Dempster.

Synopsis.

Isotopes of potassium, calcium and zinc have been determined by positive-ray analysis, using the apparatus and method previously described in which the charge deflected by a constant magnetic field through a fixed slit into a Faraday cylinder is measured as a function of the voltage accelerating the rays. Curves showing maxima corresponding to the various isotopes are reproduced. With potassium, isotopes with atomic weights 39 and 41 were found as previously observed by Aston. With pure calcium isotopes at 40 and 44, and with zinc isotopes at 64, 66, 68, and 70 were observed. After a disturbing effect of the electric field was eliminated, the ratio of the intensities obtained, 18 to 1 for the two isotopes of potassium and 70 to 1 for those of calcium, gave average atomic weights agreeing well with accepted values, 39.10 and 40.07 respectively. It is pointed out that when the determination of the relative proportions of all the isotopes of an element is made sufficiently accurate and reliable, a comparison between calculated and observed average atomic weights would give a measure of the packing effect or divergence of the weights of the isotopes from integral values. If the width of the slit used in limiting the beam of canal rays were reduced from 0.37 to .07 mm., isotopes of elements of atomic weight 100 or more should be resolved with the present apparatus.

IN the following paper the method of positive-ray analysis previously described is extended to the elements potassium, calcium and zinc. The analyzing apparatus is shown in Fig. 1 and is described in detail in two previous papers.[1] The charged atoms are formed at the right and the masses for different elements may be compared by observing the total potentials applied when they are bent so as to fall on the second slit S_2. The only alteration made in the apparatus has been to cover both sides of the slit in P with fine wires a short distance apart in order to insure that the discharge is not influenced when the electric field between P and S_1 is changed.

Experiments with Potassium (Atomic Weight 39.10).

Rays of potassium were observed from two sources. They were first found associated with sodium in some preliminary attempts to obtain rays from metals with high melting points, probably from the decomposition of water glass used in the cement on the hot anode. Two components, one much stronger than the other, were readily observed

[1] A. J. Dempster, Physical Review, 11, p. 316, 1918; Phys. Rev., 18, p. 415, 1921.

two units apart in atomic weight. A comparison with sodium located the main potassium component as close to 39. The curve in Fig. 2 shows the intensity of the rays observed as the accelerating potential was altered to bring the various parts of the bundle on to the second slit.

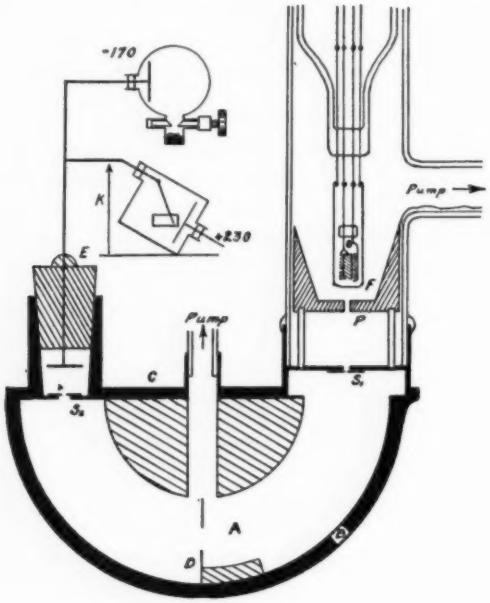


Fig. 1.

The maximum of the strong component is placed exactly at 39, and the atomic weight abscissæ are obtained by dividing 39 times 911 by the potential in volts for each measurement. The current scale for the

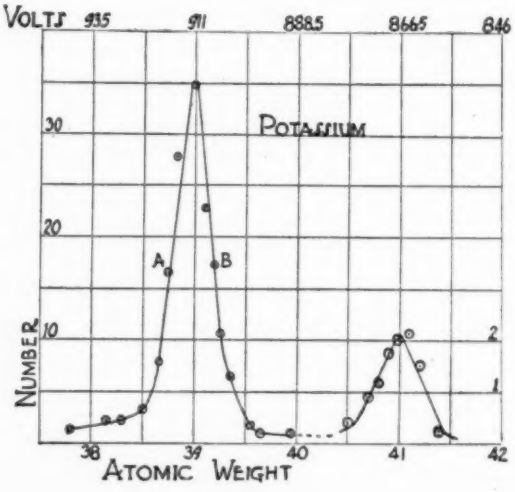


Fig. 2.

fainter isotope in the figure is made five times that for the stronger. The intensity ratio is approximately 18 to 1, giving a mean atomic mass of 39.10 in agreement with the chemical atomic weight. A possible significance of this agreement will be discussed below in connection with the measurements with calcium. Potassium rays were also measured from an anode of lithium, containing potassium as an impurity, which was heated in an iron capsule. The same two components were observed as in the case described above. The experiments thus confirm the existence of the two isotopes in potassium found by Aston with his method of analysis.[1]

EXPERIMENTS WITH CALCIUM (ATOMIC WEIGHT 40.07).

Calcium metal was found to be very suitable for use in this method of analysis. It was heated in an iron container and evaporated readily at a red heat. A strong line appeared suddenly as the evaporation commenced and was always accompanied by a faint line four units greater in atomic weight. The atomic weight 40 for the strong component was confirmed to 0.3 per cent. by comparison with a potassium line at 39 which appeared for a short time during the heating. Complete curves were drawn for the calcium lines, but as they are practically identical in form and sharpness with those in Fig. 2, they are not reproduced. The atomic masses of the two lines from calcium were compared by observing the potentials for the maxima. In Fig. 3 is shown the

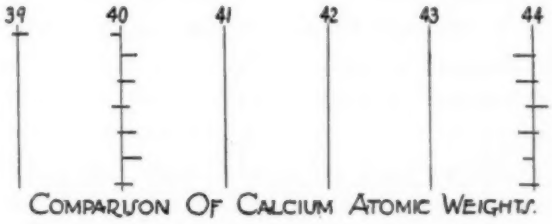


Fig. 3.

accuracy with which the observations of the maxima may be made. The center of each short line indicates the value taken as the maximum and the length of the line indicates on the atomic weight scale the estimated possible error in the setting (corresponding usually to ± 2 volts). The first two lines show the comparison with the potassium line at 39. It is seen that to the accuracy obtained the atomic weights agree with 40 and 44. With the parabola method of analysis, G. P. Thomson[2] has examined calcium rays from calcium fluoride and detected

[1] Phil. Mag., 42, p. 857, 1921.
[2] Phil. Mag., 42, p. 857, 1921.

a rather broad line around 40 in atomic weight. No isotope at 44 was observed.

The calcium used was, however, found to contain traces of calcium carbonate as an impurity, so that the rays with mass 44 might be due to carbon dioxide liberated by the decomposition of the carbonate. To avoid this uncertainty a sample of calcium was prepared by distillation in a high vacuum. Considerable quantities of gas were set free during the evaporation and continually removed by a mercury vapor pump. The calcium was condensed directly in the anode and this was then transferred to the analyzing apparatus as rapidly as possible. With the calcium thus prepared it was found that the component at 44 was still present, and was approximately 1/70 as strong as the main component. We may therefore conclude that calcium consists of two isotopes with atomic weights 40 and 44.

With the crude metal several measurements at low temperatures gave about 70 to 1 for the intensity ratio of the components, the same as found for the distilled calcium, but on increasing the temperature of the anode the component at 44 became much stronger than at low temperatures, probably due to carbon dioxide being evolved at the higher temperatures. The ratio 70 to 1 gives a mean atomic weight of 40.055, whereas the chemical atomic weight is given as 40.07. Further experiments will be necessary to obtain a more accurate value of the ratio and to examine the possibility of still fainter isotopes with other atomic weights. Accurate intensity measurements may be expected to involve considerable difficulty, since, if they are to indicate the relative proportions of the isotopes in the element, several conditions must be fulfilled; the faint background of scattered and reflected rays must be considered or suppressed, the intensity ratios must be independent of the particular experimental conditions used, the primary ionization must be unaffected by the alterations in the electric or magnetic fields used to bring a new component onto the slit, and the possibility must be considered that, as appears to hold in the case of lithium, the different components may have different rates of evaporation at different temperatures and with different surface conditions.

Ratios of Components and Atomic Weights.

It may be pointed out, however, that a reliable determination of the proportions of all the isotopes in an element by positive-ray measurements would allow conclusions to be drawn as to the existence or absence of a "packing effect" or a slight divergence of the atomic weight from an integral value. If the mean atomic weight calculated from the positive-

ray ratios, on the assumption of integral values for the components, is lower than the chemical atomic weight, we must conclude that the components have atomic weights greater than exact integers by an amount sufficient to make up the difference. Thus the agreement of the mean atomic weight obtained for potassium with the chemical atomic weight, might be used as an argument that the atomic weight of the strong potassium component is exactly 39.00 to within one integer in the second decimal place. In the case of calcium we might use the low computed atomic weight 40.055 to deduce the value $40.07 - 0.055 = 40.015$ as the correct atomic weight of the heavier component. More careful measurements of the intensity ratios will however be necessary before conclusions of this nature can have much weight.

Experiments with Zinc (Atomic Weight 65.38).

Strong rays were obtained from a zinc anode when heated to a very dull red temperature. Three strong and one faint maxima were observed, separated by two units on the atomic weight scale. It was found that the zinc lines were also obtained from a calcium anode to which a little zinc had been added. Probably due to the higher temperature the rays were then usually sharper than with pure zinc. The curve in Fig. 4 shows the different components observed with this anode. The first experiments with a zinc anode were made before those with calcium and

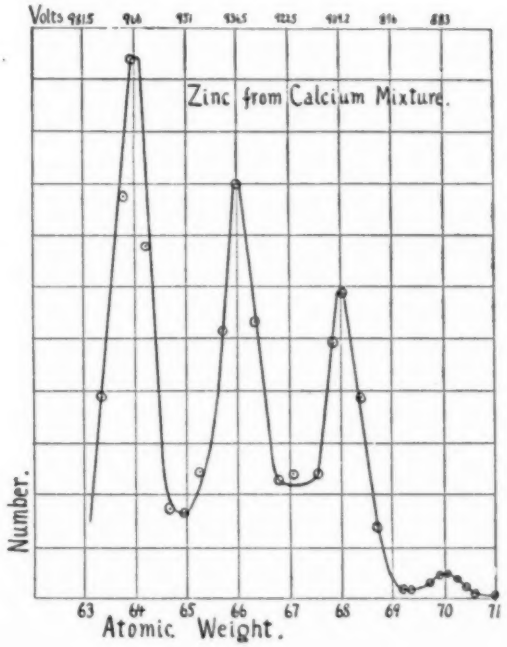


Fig. 4.

potassium, and before the two gauzes had been placed on each side of the slit in P (Fig. 1). These first experiments gave quite different intensity ratios for the components from that shown in Fig. 4, and a mean atomic weight almost a unit higher. An early curve is reproduced in Dr. Aston's book on Isotopes, p. 147. Later, with two different anodes containing mixtures of calcium and zinc, and with one containing very pure zinc, intensity ratios similar to that shown in Fig. 4 were obtained. The mean atomic weight from curve 4 is approximately 65.5.

It was suspected that the changes in the field between P and S_1, used to bring the different components on to the second slit, might have influenced the total intensity of the rays in the first experiments by means of the stray field through the slit in P. Two gauzes were therefore introduced as mentioned in the first paragraph. Intensity ratios similar to that shown in the curve were then always obtained from anodes of both pure and commercial zinc, and the total positive-ray current as indicated by a galvanometer was found independent of the field.

The accuracy with which the maxima of the three strong zinc components agreed with integral atomic weights is shown in Fig. 5. The

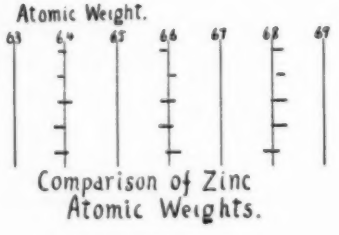


Fig. 5.

center of each short line indicates the value taken as the maximum and the length of the line indicates the estimated error in the setting (usually $\pm$ 2 volts). It is seen that to the accuracy obtained the atomic weights are two integers apart.

It was at first assumed that the atomic weights of the components were 63, 65, 67 and 69, since, with the intensities first observed, a mean atomic weight was obtained which agreed with the chemical atomic weight 65.38.[1] This reasoning was invalidated by the different intensity ratios obtained with the improved shielding, and a direct comparison with the calcium component at 40 showed the atomic weights to be near the integers 64, 66, 68, and 70. With a calcium anode to which a little zinc had been added rays of both elements were obtained, and the atomic weights could be compared by observing the potentials required to

[1] Science, Vol. 54, p. 516, 1921.

bring the different maxima on to the second slit, while the magnetic field was kept constant. The settings could usually be made with an uncertainty of 2 volts or less, and are illustrated in Fig. 6. The center

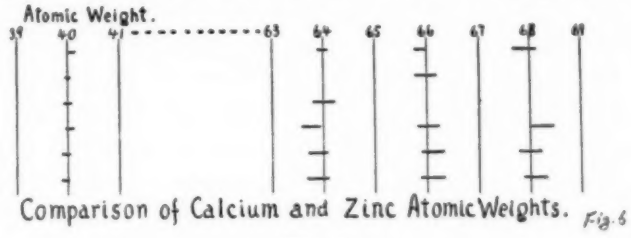


Fig. 6.

of the short line represents, as before, the value taken for the maximum and the length of the line represents the estimated error. Thus the potentials in volts used in the first plot were 974 ± 2; 610 ± 1; 592.6 ± 1; 575.1 ± 2. The first three comparisons were made with one anode and the last three with a new filling and adjustment. It is seen that within the experimental error the atomic weights of the three zinc components are 64, 66, and 68. The faint isotope at 70 was not used in the comparisons with calcium since much more time and care is required in setting on it than on the stronger components.

In all the curves drawn for the zinc rays the intensity at atomic weight 67 is greater than at 65, although the neighboring lines at 66 and 68 are weaker than 64 and 66. This is probably due to the existence of an unresolved isotope at 67, and in two curves a slight maximum was also indicated at this atomic weight. Experiments with sharper bundles will be necessary to decide definitely if a fifth isotope exists at 67 or not.

RESOLVING POWER OF THE APPARATUS.

The sharpness of the curves and the dependence on the slit width and other factors is of interest in connection with the possibility of improving the resolution sufficiently to analyze heavier elements. The slit widths used in all the experiments described in this paper were 0.37 mm. for the first, and 0.42 mm. for the second. If the focusing were perfect the width of the bundle at S_2 would be 0.37 mm. The curve in Fig. 2 is obtained as this bundle is moved from one edge of the slit S_2 across to the other, the displacement of the bundle in moving between the positions which give the currents A and B half way to the maximum being exactly the width of the bundle. From the relation M.V. = const. d^2, as discussed in the first paper,[1] we see that the beam must have had a width of 0.55 mm. in order to give the curve for potassium. The beam originally 0.37 mm. wide has thus increased in width by 0.18 mm. in

[1] A. J. Dempster, PHYS. REV., 11, p. 320, 1918.

going a distance of 17 cm. This extra width is probably due entirely to a lack of homogeneity in the velocity of the rays since a dispersion of only 3 volts in the 900 used would account for the extra width of the image. The sharpest curves observed with zinc indicate a width of 0.68 mm. at the second slit, and some experiments showed that the sharpness was affected to a considerable extent by the adjustment of the potentials between the plate P, the cathode and the anode.

If as great a uniformity in velocity can be obtained with heavier elements, as in the case of calcium or potassium, a considerable increase in resolution should be secured with narrower slits. Thus with $S_1 = 0.07$ mm. the beam should be 0.25 mm. wide at S_2 and the separation of the points AB on the atomic weight scale would be half a unit for an atomic weight of 100, so that all integral components less than this should be sharply separated. If the total potential were increased to 2,000 volts, elements as high as 200 in atomic weight should be similarly separated, provided the necessary magnetic field of 18,000 gauss could be secured.

Should it prove necessary to deal with a greater velocity dispersion than that found in the case of potassium and calcium, an electric field may be added to focus rays with slightly different velocities as in the apparatus designed by Dr. Aston. With slow rays it is also possible to combine the velocity focusing, for a single mass, with the direction focusing as used in these experiments. Figs. 7 and 8, in which A and B

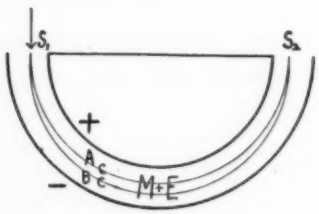


Fig. 7.

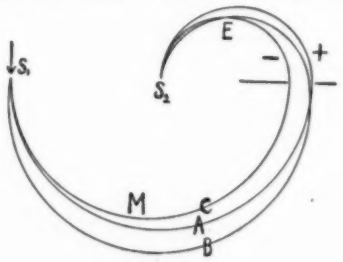


Fig. 8.

represent two rays diverging in direction, and C a ray of the same mass and smaller velocity, illustrate diagrammatically two arrangements of the magnetic and electric fields. In Fig. 7 the fields act simultaneously, and it may be readily shown that a small range of velocities is focused at S_2 when the electric force is half the magnetic and opposite in direction. In Fig. 8 the magnetic and electric fields, M and E, act separately, the velocity focusing occurring when the electric force is twice the magnetic.

The author's thanks are due to Mr. F. B. Haynes for the use of the apparatus and method he developed for distilling calcium in vacuo, and to Mr. J. K. Morse for testing the calcium chemically for carbon dioxide.

RYERSON PHYSICAL LABORATORY,
July 21, 1922.

PROPERTIES OF ROCHELLE SALT RELATED TO THE PIEZO-ELECTRIC EFFECT.

BY JOSEPH VALASEK.

SYNOPSIS.

Temperature variation of several physical properties of Rochelle salt, from − 30° to + 30° C., was undertaken to determine which of them seem to be related to the piezo-electric effect, which increases rapidly between − 20 and − 15° C. and decreases rapidly between + 20 and + 30° C. In this way it was hoped to get information as to the nature of the structure underlying piezo-electric phenomena. *Refractive indices* were measured for the three principal directions for six wave-lengths from 4554 to 6500 Å. and at temperatures of − 70, − 11.5, 0, + 21.3 and + 40° C. The variation with temperature, however, is linear, the average coefficient being 59×10^{-6} per degree. The *thermal expansion* between − 10 and + 20° C. was measured by the Fizeau method for the three principal directions. The ratio of $(n^2 - 1)$ to ρ is approximately constant, in agreement with the Sellmeir formula for dispersion, and if the change in refractivity is regarded as due to the change in density, reasonable values are obtained for the constants in the Lorentz formula. The *specific rotatory power of an aqueous solution* of the salt was found to change less than 0.4° in the interval from + 4 to 40° C., giving no indication of a change in molecular asymmetry in this interval. The value obtained at 25° C. is 25.9° for sodium light, lying between the results of previous observers. The *electrical conductivity* increases only from 2×10^{-14} mhos/cm.³ at − 65° C. to 5.4×10^{-14} at − 20° C. Between − 20° and + 30° C., however, it was found to depend on the direction of the current, being only half as great in one direction as in the other at 0° and at 20°, and above 20° it increases very rapidly to 5×10^{-9} at 43°. At all temperatures, however, the current was found proportional to the applied field, at least up to 10,000 volts/cm. *The reversible electro-optic rotation* was observed in the direction of the field, using transparent alcohol electrodes and plane polarized light of wave-length 5737 Å. At 20° the rotation of the α and β axes in their plane per unit field normal to them is 1.7×10^{-4} degrees, and decreases for higher temperatures much as the dielectric constant does. The electro-optic constant e_{41} was also computed. Although Rochelle is classed as a type of crystal that should show no *pyro-electric effect*, a "real" effect was observed in the ă crystallographic direction as the crystal was gradually heated at a constant rate. The coefficient changes sign just below room temperature and becomes very large.

Theory of piezo-electricity is discussed briefly in the light of these results. In view of the fact that none of the properties measured show changes with temperature which correspond with those of the piezo-electric effect it is probable that the elastic or piezo-optic constants must change in such a way as to account for the piezo-electric changes.

Newman's Principle of Symmetry in Crystal Optics.—Rochelle salt, if it belongs to the hemihedral class of the orthorhombic system, seems to form an *exception* to this principle since most of its electrical properties in the direction of the ă axis depend on the direction of the field.

Infra-red absorption band for Rochelle salt is computed from the constants of the dispersion formula to be at about 55 μ.

THE experiments herein described were initiated for the purpose of examining some of the properties of Rochelle salt which might be related to the piezo-electric property and thus to obtain further information on the nature of the structure underlying piezo-electric phenomena. Rochelle salt is particularly suited for this study because its piezo-electric reaction is relatively large and because of the marked changes which occur in its activity at certain temperatures. As the crystal is heated from low temperatures, there is a sudden increase in activity between -20 and $-15°$ C. and a corresponding decrease between $+20$ and $+30°$ C. as the following table shows. The piezo-electric modulus given here is defined as the electric polarization in the a crystallographic direction per unit shear in the plane normal to it.

TABLE I.

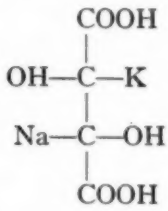
Temperature.	Piez. Modulus.
$-70°$ C.	0.017×10^{-8}
-50	0.017
-30	0.065
-20	1.08
-10	6.07
0	6.75
$+10$	7.42
$+20$	8.10
$+30$	1.08
$+40$	0.41

In those temperature intervals where the piezo-electric property makes rapid changes, the writer has undertaken to study various other physical properties of the crystal. In the first place the variation with temperature was studied with the thought that the same type of structure may be responsible for both the piezo-electric property and the optical rotation or that they may be related in some way. Then again measurements were made on the indices of refraction because a shift in an absorption band caused by a changing restoring force of the ions producing the piezo-electric effect would be reflected in the indices of refraction if the absorption bands involved were not too far away from the visible region. Furthermore, observations were made on the reversible electro-optic effect.

We shall begin by reviewing some general facts concerning Rochelle salt. This substance is a double tartrate of sodium and potassium with the chemical formula $NaKC_4H_4O_6 \cdot 4H_2O$. It crystallizes in the ortho-rhombic system, showing sphenoidal hemihedrism. It is optically active both as a crystal and in solution. It is, of course biaxial, as the crystal

[1] Valasek, PHYS. REV., XIX., 478, 1922.

system shows. The structural formula is



This form has the usual type of asymmetry occurring in optically active carbon compounds. The crystal is brittle and soluble in water. This latter property enables one to cut it by a wet string running over pulleys and through water, and to polish it on a slightly moistened piece of ground glass. Since it cracks very easily due to unequal or too rapid temperature changes, it must be handled carefully. It cannot be heated above 53° C. as it transforms here into water and the single tartrates of sodium and potassium with an absorption of heat. A moderately sensitive differential thermocouple scheme indicates no sharp heat transformation anywhere between − 70 and + 54° C. On heating, however, there begins a slow and steady apparent heat evolution at 24° C. which continues up to 53° C. This is thought to be due to either an increase in thermal conductivity or to a steadily decreasing specific heat.

REFRACTIVITY.

The three principal indices of refraction were determined by a prism and spectrometer method for a number of wave-lengths. For measurement at various temperatures the crystal was mounted on a pedestal about ten centimeters high so as to be in the center of the double-walled vessel which contained the heating or cooling mixture. A cross-section of this arrangement is shown in Fig. 1*A*. Tubes *A* and *B* (1 x 2 cm.) served as passages for the light between the collimator and the telescope. Diaphragms *C* and *D* together with end plugs and plane-parallel windows served to cut down air circulation. The copper-constantan thermocouple which measured the temperature came up to the crystal through the hollow pedestal, which was largely made of thin-walled glass tubing. The cold junctions were kept in ice and the electromotive force was measured by a Leeds and Northrup Type K potentiometer. The thermocouple was calibrated at the fixed points given by fresh liquid air, frozen mercury, ice, and steam.

The prism used was cut from a large crystal about five centimeters along each edge, in such a way that one of the faces was a natural crystal face while the other was nearly parallel to the b and c crystallographic

axes (Fig. 1*B*). In order to procure faces as flat as possible, a large prism was first cut and polished. From its center was cut the small prism about 2 cm.^{3}, which was used in the experiments. Diaphragms of black paper served to still farther cut down the areas of the faces, care being taken not to decrease the resolving power so much as to cause a noticeable lack of precision in setting on the spectrum lines. In this way a good double spectrum was obtained from which two indices could be determined. These indices will be denoted by n_1 and n_2 in the order of their magnitude.

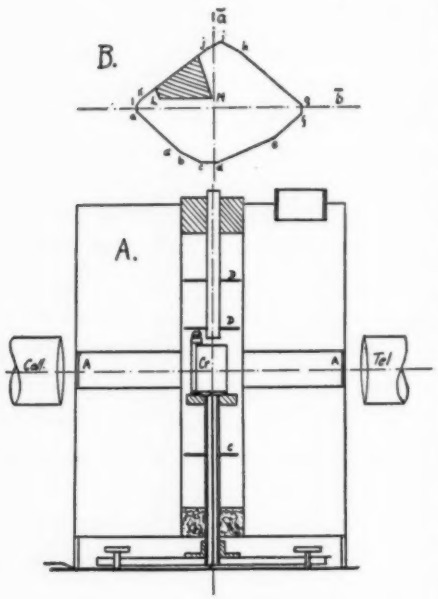


Fig. 1.
Mounting of prism for refractivity measurement.

The source of light was an arc between carbons containing barium chloride. This source gives a set of six bright lines fairly well distributed throughout the spectrum and proved to be very convenient for the determination of dispersion.

In calculating the three main indices, Fresnel's formulæ for inactive crystals were used in spite of the fact that Rochelle salt is active.[1] This is permissible in this case because the indices were not measured closer than five units in the fifth decimal place and because the rotatory power of the crystal produced much smaller deviations from Fresnel's formulæ. Following Pockel's *Krystalloptik*, α, β, and γ will be used to denote the three main indices in the order of increasing magnitude and ν_1, ν_2, and ν_3 to denote the direction cosines of the wave normal in the crystal with respect to the principal axes. The indices n_1 and n_2 in an equatorial plane $\nu_1 = 0$, that is, normal to the α axis of the index-ellipsoid, will be given by the two n roots of the equation:

$$\left\{\frac{1}{\alpha^2}-\frac{1}{n^2}\right\}\left\{\left(\frac{1}{\gamma^2}-\frac{1}{n^2}\right)\nu_2^2+\left(\frac{1}{\beta^2}-\frac{1}{n^2}\right)\nu_3^2\right\}=0. \qquad (1)$$

In this plane, one of the indices, namely $n_1 = \alpha$, should be the same in all directions. This was found to be accurately true and is taken to justify our use of the simpler formula.

The orientation of the crystal was roughly as shown in Fig. 1 *B*, the

[1] Pockels, Krystalloptik, 31.

LM face being normal to the ă axis within three degrees as determined from the crystal angles. The middle and greatest indices were calculated from formula (1) by solving for β and γ when measurements of n_2 had been made for two known directions. The value of β so found differed by only 0.00002 from the value of n_2 normal to the face LM. The two directions chosen were normal to the faces of the prism.

The crystal was clamped in place by the edge facing the collimator so that when its angle changed due to anisotropic expansion[1] the light would still be normally incident on this face. If the constants for the two directions are respectively unprimed and primed, the following set of formulæ give the indices:

$$n_1 = \frac{\sin A_1}{\sin (A_1 + D_1)}, \quad \text{etc.},$$

$$\alpha = n_1 = n_1',$$

$$\beta^2 = \left(\frac{\nu_3}{\nu_2\nu_3' - \nu_3\nu_2'} \right) n_2' - \left(\frac{\nu_3'}{\nu_2\nu_3' - \nu_3\nu_2'} \right) n_2, \qquad (2)$$

$$\gamma^2 = \left(\frac{\nu_2}{\nu_2\nu_3' - \nu_3\nu_2'} \right) n_2' - \left(\frac{\nu_2'}{\nu_2\nu_3' - \nu_3\nu_2'} \right) n_2.$$

The angles of the prism A and the angles of deviation D were measured on the spectrometer by standard methods at a number of steady temperatures between -70 and $+40°$ C. A nicol prism was used in front of the eyepiece to keep the two spectra distinct.

A set of careful determinations of the three indices was made in this way for the six lines of the barium spectrum at room temperature with the windows of the cooling chamber removed. These are given in Table II.

TABLE II.

Temperature 21.3° C.

Wave-length.	α.	β.	γ.
4554.2 Å.....	1.49906	1.50062	1.50504
4934.2	1.49565	1.49734	1.50154
5535.7	1.49170	1.49348	1.49721
5853.9	1.49001	1.49183	1.49540
6141.9	1.48878	1.49056	1.49430
6497.1	1.48743	1.48920	1.49280

The directions of the α, β, and γ axes of the index ellipsoid are respectively the same as the directions of the c, $\bar{\text{b}}$, and ă crystallographic axes.

Above and below room temperature, coverglasses cemented on with

[1] Voigt, Krystallphysik, 276.

Canada balsam had to be applied to preserve the polish of the prism. With the apparatus entirely assembled another set of determinations was made at the same temperature and corrections found for the cover-glasses and windows. The indices were then measured for steady temperatures of -70, -11.5, 0.0, $+21.3$, and $+40°$ C. The angle of the prism at these temperatures was measured by a reflecting eyepiece.

The main indices were calculated and plotted and it was observed that their variation with temperature was practically linear. From the best set of straight lines through the points the following values were obtained for the indices at 0° C. and for the temperature coefficients.

TABLE III.

Wave-length.	Indices at 0° C.	Temp. Coefficient.
	1.5004	0.000064
4554.2	1.5019	58
	1.5063	68
	1.4970	63
4934.2	1.4987	58
	1.5029	65
	1.4930	64
5535.7	1.4947	58
	1.4986	63
	1.4913	61
5853.9	1.4930	60
	1.4968	58
	1.4900	61
6141.9	1.4917	58
	1.4953	61
	1.4888	63
6497.1	1.4905	59
	1.4939	59

The values of α and β in both tables are more accurate than those of γ because the latter are obtained by solving the equation of the oval for its major axis which is respectively about 90° and 40° from the directions of the radii measured. In Table II. the values of α and β are good to $\pm$ 0.00005, while γ is good to $\pm$ 0.00015. The values in Table III. may be in error by greater amounts because of the greater variety of chances for error that present themselves in measurements at other than room temperature.

A surprising outcome of these measurements is that there is no marked change in optical properties between -70 and $+40°$ C. This was contrary to expectation and shows that there is no gross change in crystal structure occurring between these temperatures. This eliminates one explanation that may be advanced for the variation in piezo-electric response that occurs in this range.

Drude's dispersion theory applied to this data gives a little information as to the nature of the bound charges. The best set of observations for this purpose is the α set given in Table II. since it is checked by a greater number of independent observations and is a directly measured result. Suppose we take the five-constant formula:[1]

$$n^2 = -B'\lambda^4 - A'\lambda^2 + A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}. \tag{3}$$

According to the theory the constants should all be positive and respectively given by the formulæ:

$$B' = \sum \frac{\theta_r}{\lambda_r^2}; \qquad A' = \sum \frac{\theta_r}{\lambda_r^4};$$
$$A = 1 + \sum \theta_v; \qquad B = \sum \theta_v \lambda_v^2; \qquad C = \sum \theta_v \lambda_v^4, \tag{4}$$

where the subscript r means that the summation is to be carried out only for charges whose free period lies in the infra-red, while v refers in a similar fashion to the ultraviolet charges, and θ is the contribution of each type to the dielectric constant. If there is only one predominating type of each, the summation signs can be removed and we have

$$\lambda_r^2 = \frac{K - A}{A'}, \tag{5}$$

where K is the ordinary dielectric constant and

$$K = 1 + \sum \theta_v + \sum \theta_r = A + \sum \theta_r. \tag{6}$$

Evaluating the constants of (3), it is found that

$$B' = -0.163,$$
$$A' = +0.215,$$
$$A = +2.282,$$
$$B = -0.007,$$
$$C = +0.002.$$

Since K has the value 645 at 20° C., it is found that the infra-red absorption band should be at 55 microns.

[1] Drude, Optik,

Inspection of the values above shows that the constants B and B' have the opposite sign to that which the theory gives. The observations are considered to be fairly reliable as measurements on several crystals show, so that the sign is not due to error.

In a previous paper the writer has calculated the position of an absorption band from piezo-electric data.[1] The expression used was derived on the assumption that $\alpha = 1/3$, where this α is defined by the relation $E = E_p + \alpha P$, and E_p is the field at a charge in a medium whose polarization is P. It will be shown in the following that α is far from $1/3$ for Rochelle salt, but that this constant can be eliminated anyway. The equation for the X component of vibration of an ion of charge e and mass m is:

$$m\ddot{\xi} = eX - 4\pi e^2\left(\frac{1}{\theta} - \alpha N\right)\xi. \tag{7}$$

The wave-length of the free vibration is then

$$\lambda = \left\{\frac{c^2\pi m}{e^2}\left(\frac{\theta}{1 - \alpha N\theta}\right)\right\}^{1/2}. \tag{8}$$

If the contribution of this ion to the dielectric constant is K_r and there are N such ions per cubic centimeter, then

$$K_r = 1 + \frac{N\theta}{1 - \alpha N\theta} \tag{9}$$

and we have

$$\lambda = \left\{\frac{c^2\pi m(K_r - 1)}{Ne^2}\right\}^{1/2}, \tag{10}$$

which is independent of α but contains K_r. Since this is very nearly equal to the entire dielectric constant between -20 and $+20°$ C., we shall replace K_r by K. The difference between these two quantities is the constant A of the dispersion formula and K is well in the hundreds at these temperatures. The quantities N, m, and e are unknown, but it should be interesting to try some possible values. For convenience let us rewrite the expression by putting S equal to the sum of the atomic weights of the atoms in this ion, letting σ be the sum of the chemical valencies, and u be the number of such ions in each molecule. Then we have:

$$\lambda_r = 0.741\sqrt{\frac{(K - 1)S}{\sigma^2 u}}. \tag{11}$$

Since the infra-red ions are always of atomic or molecular magnitudes

[1] PHYS. REV., XIX., 489.

and because the water of crystallization is so important to the piezo-electric properties, it may be that either the O or the OH ion is the important one. Taking the value of K as 645 at 20° C., it is found that the natural wave-length for the two cases above is respectively 9.5 and 40. The latter gives the better agreement with the value found from the dispersion theory. It must be admitted that there are many arbitrary assumptions in the above. This, however, is as much as can be done at present.

The temperature coefficients of the indices given in Table III. turned out to be relatively large. This would ordinarily mean that the coefficient of volume expansion is large. On either Drude's or Lorentz's dispersion theory, the variation in the indices of refraction of any single chemical compound should be dependent entirely on the variations in the numbers of dispersion charges per unit volume. This number varies inversely as the density. The Lorentzian relation[1] between index of refraction n and density ρ may be written in the following form:

$$\frac{1}{\rho} = \frac{C}{n^2 - 1} + C\alpha, \tag{12}$$

where

$$C = \frac{1}{\rho}\sum \frac{\nu_s^2 e_s^2}{m_s(p_s^2 - p^2)}. \tag{13}$$

Knowing n and ρ at various temperatures enables one to find the constants C and α and to test the theory.

THERMAL EXPANSION.

To find the variation in specific volume with temperature, the coefficients of linear expansion were measured in the three principal directions by the Fizeau method.[2] A plan of the apparatus is shown in Fig. 2. The three tripods which supported the optical surfaces were made of iron so as to expand very much less than the crystal. A thermocouple T.C., whose junction nearly touched the crystal, was used to measure the temperature. The movement of the rings between two steady temperatures was observed in the telescope Tel. The apparatus had to be sealed to exclude moisture; otherwise this would condense on the small tripod points p and cause them to sink in. The way this occurred is interesting. The inset in Fig. 2 shows a cross-section of one of the pits.

In each of the crystallographic directions a set of measurements of the relative expansion of crystal and apparatus was made for the temperature

[1] Richardson, Electron Theory, p. 148.

[2] Tutton, Crystallography, p. 884.

interval of − 10 and + 20° C. using a cube of Rochelle salt. The dimensions of the cube were: 1.302 × 1.271 × 1.163 cm. and its faces were cut and polished within 3° of normal to the crystallographic axes. The expansion of the apparatus was measured by using a cube of lead whose coefficient was taken to be 0.00002726. This cube was cut from a Bureau of Standards melting point sample and was nearly pure. The average coefficients of expansion between − 10 and + 20° C. for Rochelle salt were thus found to have the values:

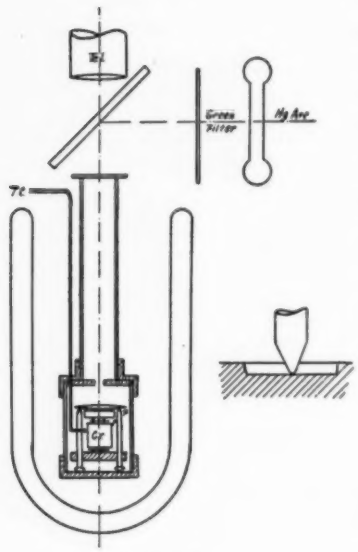


Fig. 2.
Dilatometer.

$$a = 0.0000599 \pm 4,$$
$$b = 0.0000381,$$
$$c = 0.0000448.$$

The coefficient of volume expansion is accordingly:

$$\Delta = 0.0001428.$$

Since the density of Rochelle salt at 0° C. was found to be 1.766 we have for any other temperature; θ°C:

$$\delta = 1.766 - 0.0002522\,\theta.$$

As noted above these values are the averages over a temperature range of thirty degrees extending from − 10 to + 20° C. Lower temperatures could not be conveniently kept steady for a long enough period of time, while at higher temperatures there was trouble due to condensation of traces of moisture on the crystal as soon as the surroundings were warmed. Unless the end temperatures were steady for about half an hour one could not obtain very reliable results as it took that long to be sure that the fringes were perfectly steady. It was desirable, however, to see if a change in dimensions could be detected at − 20° C. where the crystal became active. Observation of the movement of the fringes during a slow and uniform rate of heating of 2° per minute from the temperature of carbon-dioxide snow gave a smooth curve for all three crystallographic directions. There can be no abnormal change in dimensions comparable with the wave-length of mercury-green light unless this is spread out over a range of about ten degrees or more.

According to the Lorentz formula (12) there is a linear relation between

$1/\rho$ and $1/(n^2 - 1)$. This gives a set of three straight lines for any one wave-length, whose slopes are C_1, C_2, and C_3, and whose y intercepts are $C_1\alpha_1$, $C_2\alpha_2$, $C_3\alpha_3$. The values of α are of interest as bearing on the effect of surrounding polarization on the dispersion charges. For a cubical arrangement of charges it is found to be equal to one third. Drude, in his dispersion theory, assumes that the force on the dispersion charges is equal to the electric vector of the incident wave times the charge, that is, he puts α equal to zero. This theory leads to the Sellmeier type of formula. Lorentz's formula differs from this only in so far as no assumptions have been made regarding the value of α.

The values of C and α given by the best straight lines through the calculated points are as follows:

TABLE IV.

Wave-length.	C.	$\frac{n^2 - 1}{\rho}$.	α.
	0.706	0.716	0.003
4554.2	0.729	0.710	0.080
	0.660	0.707	0.068
	0.660	0.705	0.043
5535.7	0.718	0.698	0.078
	0.657	0.695	0.043
	0.648	0.696	0.041
6497.1	0.673	0.690	0.021
	0.683	0.689	0.017

The values of α are evidently much nearer zero than one third and the dispersion should be fitted fairly well by Sellmeier's formula. The values of C roughly agree with $(n^2 - 1)/\rho$ as the table shows. This agreement should be perfect when α is zero.

The values of C and α above are calculated so that the variation of the index of refraction with temperature is accurately accounted for by the dilatation of the crystal. Since their values are not unreasonable, at least the bulk of the change in indices can be so accounted for.

The variation in C must be all due to changes in the natural period p_s for any one color. The above values show that the absorption bands for the three principal indices are substantially the same in the infra-red but may differ in the ultraviolet. The small α means that the force on a unit charge per unit polarization is small, just as though the charge were well shielded.

OPTICAL ACTIVITY.

Since the optical activity and piezo-electric property always occur simultaneously in crystals having an asymmetric structure, it was decided to study the optical activity of Rochelle salt. Substances forming such crystals may be rotatory when dissolved or melted, like Rochelle salt and sugar, or they may be only active in the crystalline state, like quartz. If they are active in the non-crystalline condition, it is due to an asymmetric molecular structure. Such substances are as a rule carbon compounds and the asymmetry may be pictured by a structural formula in space in which the four radicals combined with the carbon atom are placed at the corners of a tetrahedron. J. J. Thomson[1] has shown that in the case of active solutions the molecules must have both dynamic and electric asymmetry, while in a crystal either type is sufficient to produce activity.

There is reason to believe that the piezo-electric property is rather due to inter-molecular reactions in the crystal structure, so that naturally, it would be best to measure the rotatory power of the crystal in the directions of the optic axes. This has been done at ordinary temperatures by Pocklington[2] and is the first such determination for a biaxial crystal. He found that the plane of polarization of sodium light was rotated $-1.2°$ per millimeter in the directions of both binormals. This work was repeated and extended to other crystals by Dufet, who found for Rochelle salt -1.35 instead of -1.2. There is difficulty in carrying out such measurements at different temperatures because of the movement of the optic axes.

The rotatory power of the solution can, however, be measured without much difficulty, but the range of temperatures is very limited and covers only that one of the critical points which is at room temperature. At any rate some alteration in molecular structure may be detected here. One may suppose, moreover, that a change in molecular structure would be the basis of any change in crystal structure.

Observations were accordingly made on the rotation by a solution of a crystal of Rochelle salt in water. A ten-centimeter polarimeter tube was inserted in a double-walled chamber which could be filled with water and heated electrically. The temperature was measured by a copper-constantan thermocouple whose junction was tied to the center of the polarimeter tube. The brass ends of the tube were coated by a thin film of paraffin to keep the solution from attacking them and becoming contaminated.

[1] J. J. Thomson, Phil. Mag., Dec., 1920.

[2] Pocklington, Phil. Mag. (6), II., 368, 1901.

The concentration of the solution was determined by evaporating a carefully weighed portion in a hot water bath and then drying the residue under a bell-jar with P_2O_5 in vacuo until the weight showed no further diminution. The remainder was assumed to be the anhydrous salt. The concentration used was 0.264 grams of the anhydrous salt per cubic centimeter of solution at 4° C. The density of the solution decreases by about a half per cent. between 4 and 30° C. Effects of expansion of the polarimeter tube are negligible.

The specific rotations for sodium light are shown plotted against temperature in Fig. 3.

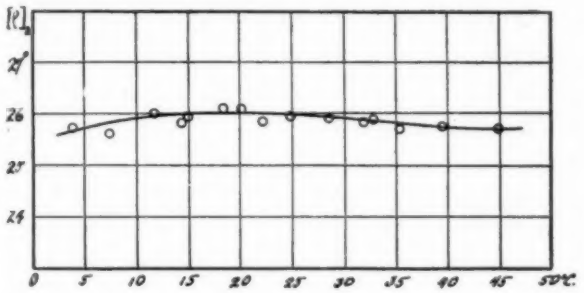


Fig. 3.

There seems to be a considerable lack of agreement between values given by various investigators for the rotatory power of Rochelle salt solution and the present value does not agree with any of them. In Dufet's tables the following figures are given:

$[\rho]_D$	Concentration.	Authority.
22.42.....	c = 20 hydr.	Krecke, 1872.
29.67.....	c = 10.77 anh.	Landolt.
29.5.....	c = 21.0 anh.	Kummel, 1891.
29.53.....	c = 9 to 43 anh.	Thomsen, 1886.
22.12.....	c = 5 to 45 anh.	Long, 1888.

The concentration is given in grams per one hundred cubic centimeters of solution. The present value comes just between the two extremes.

The differences can hardly be due to error in measuring the rotation so that it seems that they must be due to differences in taking care of the water of crystallization in calculating the concentration, or possibly due to a very impure salt. The writer has also checked his result by measuring the rotation by a weighed amount of hydrated Rochelle salt in a weighed amount of water. The weight of the water of crystallization was calculated from molecular weights and subtracted from that of the

salt and added to that of the water. Using the density of water the grams of anhydrous salt in a cubic centimeter of solution was found. The final results were 26.4 and 25.8 on two different trials.

In conclusion, however uncertain the value of $[\rho]$ is, it is at least evident that no marked change in rotatory power occurs at 20° C. The molecular structure which accounts for optical rotation is therefore independent of the piezo-electric structure.

ELECTRICAL CONDUCTIVITY.

In a recent paper the writer has reported a variation in electrical conductivity of Rochelle salt with temperature.[1] It appeared that there was a very marked and continuous increase in conductivity beginning at 23° C. when the crystal was heated at a uniform rate from the temperature of carbon-dioxide snow. Under normal conditions the crystal was about as good an insulator as ordinary glass when the surfaces were dry and the temperature was less than 23° C. There has been recently reported [2] an increase in conductivity for alternating currents even at temperatures below 23° C. when the field exceeds about 3,500 volts per centimeter. In view of this it seemed advisable to extend the writer's work on conductivity for direct currents by making measurements for various applied fields at different temperatures.

The conductivity was determined by measuring the current through the crystal by a sensitive galvanometer and the voltage across it by an electrostatic voltmeter. The galvanometer was of 650 ohms resistance and was shunted by 20,000 ohms so as to be nearly aperiodic. Its sensitivity under this condition was 1.108×10^{-9} amperes per millimeter deflection.

The direct electromotive force was furnished by a transformer giving up to 10,000 volts in connection with a rectifier. A Coolidge tube proved convenient for rectification since the current was only enough to take care of insulation leakage. The diagram of connections is shown in the figure below. The battery of Leyden jars across the terminals was of sufficient capacity to keep the system charged for several seconds after the transformer was cut off.

The leads were soldered to the tinfoil plates which were cemented to the crystal with shellac. To one of the plates there was also soldered a copper-constantan thermocouple to measure the temperature of the crystal. To help reduce errors due to surface leakage, the tinfoil plates did not extend closer than two millimeters from the edges of the plate.

[1] PHYS. REV., XIX., p. 488.

[2] J. G. Frayne, Wash. Meet. of Am. Phys. Soc., April, 1922.

The surfaces were dried by phosphorus pentoxide and then coated with paraffin. The sample so prepared was suspended by the leads in the center of a large glass test tube. The wires were sealed through glass tubes which passed through the stopper. Diaphragms, wool plugs, and a brass cylinder helped to keep the temperature uniform. The tube containing the crystal was cooled by cold packs or baths or heated by the electric heater which surrounded it.

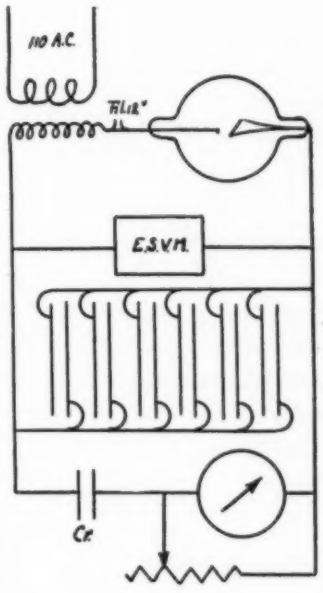


Fig. 4.

It was soon realized that when the applied potential became too great there was a corona discharge off the edges of the tinfoil. The first noticeable increase in conductivity due to this cause came at about 12,000 volts per centimeter through the crystal. There is reason to believe that the apparent increase in conductivity for alternating fields in the work referred to above is due to corona unless special precautions were taken to eliminate it. Experiments show that the corona loss may start at much lower potentials if the electrode edges are not separated or protected in some way.

For Rochelle salt it was found that no marked increase in conductivity or other deviation from Ohm's law occurs below 10,000 volts per centimeter and probably none below double that field.

The conductivity was found to depend on the direction of the current for some temperatures. This occurred in the range of maximum piezoelectric activity, the greater conductivity being in the direction, (+), of the permanent polarization.[1] Even in this case the relation of current to field was linear within the above field limits.

TABLE IV.

Temperature.	Conductivity.
− 65° C.	2.0×10^{-14} mhos/cm.[3]
− 40	3.6×10^{-14}
− 20	5.4×10^{-14}
0	$+ 9.0 \times 10^{-14}$ and $- 5.0 \times 10^{-14}$
+ 20	$+ 22.0 \times 10^{-14}$ and $- 11.0 \times 10^{-14}$
+ 30	$+ 11.8 \times 10^{-13}$ and $- 11.1 \times 10^{-13}$
+ 35	1.00×10^{-11}
+ 43	5.00×10^{-9}

[1] PHYS. REV., XVII., p. 476.

Values at higher temperatures will be found in one of the writer's papers.[1]

In the paper just referred to, it was reported that the crystal begins to conduct at 23° C. What was really meant was that conduction below this temperature seemed negligible. This, of course, depends on the sensitivity of the instruments used and on the scale in plotting curves. By changing these, apparently sharp bends in exponentially increasing curves may be put nearly anywhere. As the above table shows, there are no sharp breaks in the conductivity curve.

It is interesting that the conductivity is different for currents in opposite directions in the temperature range where the crystal is piezo-electrically active. The significance of this is not fully understood but it seems to be connected with the permanent polarization and related polar effects as will be pointed out in the concluding discussion. If the polarization were not so small, this would be in accordance with Thomson's theory of conduction, the essential feature of which is the shooting of electrons from atom to atom by a sort of radio-activity induced by the field.

ELECTRO-OPTIC EFFECT.

The reversible electro-optic effect in acentric crystals has been studied for several substances, including Rochelle salt, by F. Pockels.[2] These types of crystal are always piezo-electric and exhibit an electro-optic effect analogous to the Kerr effect except that the polarization constants vary in a linear manner with the field instead of the square. Pockels' observations have considerable theoretical interest because he was able to show that the effect is only partly due to the mechanical action of the electric field and that there is a part due to a direct influence of the applied field on the vibrations of the charges in the medium. This change in the periods, which is analogous to the Stark effect, affects the optical properties of the substance.

To completely determine any general variation in the optical properties of a crystal, the positions and magnitudes of the three main indices must be fixed. This may be done by six quantities called polarization constants or optical parameters.[3] Pockels develops a set of formulæ by first writing the most general expression for each of these parameters in the form of a power series in ascending powers of either the field or the polarization. The reversible electro-optic effect must be expressible in odd powers alone, and for fields not too great, this may be taken as the first. This effect is observed in all acentric crystals and in no other

[1] PHYS. REV., XIX., p. 488.

[2] Pockels, Krystalloptik, p. 492, and Voigt, Magneto- u. Elektro-optik, p. 341.

[3] Pockels, Krystalloptik, p. 66.

types. The irreversible or Kerr effect must be an even function of the field and as a first approximation, the first may be taken. This effect is observed in all substances but needs a relatively greater field to bring it into prominence. These general formulæ are then simplified by considering the symmetry of the particular crystal system to which they are to be applied. This is done by adjusting the coefficients so as to put the equations into such a form that transformations of the axes into physically equivalent positions keeps their form invariant. These physically identical positions are found by a consideration of crystal symmetry which is their most general manifestation. The equations for the hemihedral class of the orthorhombic system are:

$$\begin{aligned} a_{11} &= a_0^2; \qquad a_{22} = b_0^2; \qquad a_{33} = c_0^2. \\ a_{23} &= e_{41}P_x; \qquad a_{31} = e_{52}P_y; \qquad a_{12} = e_{63}P_z. \end{aligned} \tag{15}$$

In these equations a_{11}, etc., are the six polarization constants; a_0, b_0, c_0 are the initial values of the principal wave-velocities; P_x, P_y, and P_z are the components of the polarization, which is assumed to be a linear function of the field, and e_{41}, e_{52}, and e_{63} are the three remaining constants which describe the electro-optic behavior of this class. These formulæ show that since the first three parameters do not change, the only effect in this type of crystal is the rotation of the principal axes around the lines of force. If the components of the rotation are ϕ_x, ϕ_y and ϕ_z then

$$\tan 2\phi_x = \frac{2a_{23}}{a_{22} - a_{23}}, \qquad \text{etc.,}$$

or

$$\tan 2\phi_x = \frac{2e_{41}P_x}{b_0^2 - c_0^2} = \frac{K_x - 1}{2\pi(b_0^2 - c_0^2)} \cdot e_{41}X. \tag{16}$$

Values given by Pockels to the constants of Rochelle salt are:

$$e_{52} = -10.8 \times 10^{-8}; \qquad e_{63} = +2.1 \times 10^{-8}.$$

He remarks that the value of e_{41} could not be definitely determined because of the strong internal conductivity in this direction, but still that it was found to be negative and of the same order of magnitude as e_{52} or perhaps greater. In some cases of other crystals he was able to calculate how much of the effect was due to electric deformation, but in the case of Rochelle salt the necessary data on elastic constants and piezo-optic coefficients was lacking. The sign of e_{63}, however, is opposite to what it would be if all the effect were due to electric deformation so that there is surely a direct electro-optic effect in this case at least.

In the ă direction Pockels found also an increase in double refraction,

i.e., a Kerr effect, and states that this might be related to the large internal conductivity in this direction. The conductivity of the crystal is, however, not particularly large under ordinary conditions as the preceding pages show.

The present work is concerned with the variation in the electro-optic effect near the upper, more accessible, critical piezo-electric temperature range. Whereas Pockels calculated the rotation of the principal axes by observing the change in double refraction in some known direction in the plane normal to the field, the writer sought to measure the effect more directly. The most convenient arrangement was considered to be one in which transparent electrodes were applied to the faces of the crystal so that observations could be made in the direction of the lines of force. For this purpose, alcohol electrodes were used since this substance does not dissolve the crystal while its conductivity is 10^5 times as great as that of Rochelle salt at the temperatures employed. The arrangement used in mounting the crystal plate is shown in Fig. 5. A difference of

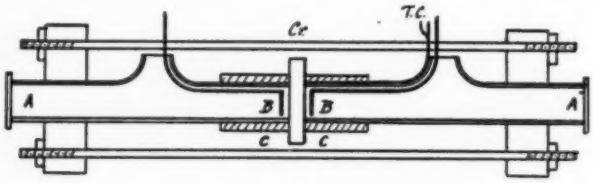


Fig. 5.

potential was applied between the platinum rings *BB* which were near the crystal and in the tubes containing the alcohol. The crystal was clamped between the rubber tubes *CC* by the screws *DD* running through the hard rubber blocks *EE*. The plane-parallel windows *AA* were cemented on with paraffin. A thermocouple T.C. came under one of the rubber tubes close to the crystal. To minimize electrical leakage over the surfaces the plate was made as large as possible so as to present a maximum distance around the edges. The alcohol had to be free of water so as not to spoil the faces of the plate. The difference of potential was applied and measured by the same scheme as used in the conductivity measurements.

The monochromatic light used in the measurements was furnished by a Hilger wave-length spectrometer in connection with an arc light. For most purposes the brightest illumination obtainable gave the best results. This proved to be the yellow-green of 5737 Å. A lens and nicol prism were placed in the beam so that plane polarized parallel light could be transmitted through the crystal plate in the direction of the applied field. The resulting elliptically polarized light was analyzed

by A. Q. Tool's modification[1] of Stokes's analyzer which was kindly loaned to the writer by the University of Nebraska.

For any crystal plate with relative retardation δ and orientation ϕ with respect to the plane of polarization of the incident light, the angle ω whose tangent is the ellipticity is given by the equation:

$$\sin 2\omega = \sin 2\phi \sin \delta. \tag{17}$$

For a Stokes's analyzer of compensator order πN_1 which is set on this ellipse we have:[2]

$$\sin 2\omega = \sin 2\pi N_1 \cos n,$$

where

$$\cos 2\pi N_1 = \frac{\tan n}{\tan c} \tag{18}$$

and n and c are respectively the differences between complementary compensator and nicol settings. Combining these two equations and differentiating, we find that:

$$-\sin 2\pi N_1 \cdot \sin n \cdot \Delta n = 2 \cos 2\phi \cdot \sin \delta \cdot \Delta\phi + \sin 2\phi \cdot \cos \delta \cdot \Delta\delta. \tag{19}$$

Suppose that the plate is set so that $\phi = 0$. Then if the compensator is very nearly a quarter wave plate and the ellipticity is small so that n is nearly $\pi/2$, we have as more or less of an approximation according to the accuracy with which these conditions are fulfilled:

$$\Delta n = 2 \sin \delta \cdot \Delta\phi. \tag{20}$$

The relative retardation δ can be calculated from the indices and the thickness of the plate. For the best accuracy the thickness should be such that $\sin \delta$ is nearly unity. The value of δ is given by:

$$\delta = \frac{2\pi d}{\lambda}(n_1 - n_2). \tag{21}$$

For light of wave-length 0.00005737 cm., δ is equal to 19.75 d, so that d should best be 2.00, 2.15, 2.31, 2.47, etc., millimeters and not 2.39, 2.55, etc. At the proper thickness a change in δ has a negligible effect on Δn as equation (19) shows. By choosing such a thickness, errors due to temperature and ordinary electro-striction are eliminated.

A suggestion for improvement in apparatus and method is to mount the crystal on a graduated circle, and, having set the analyzer for plane polarized light, find the rotation of the crystal necessary to restore it. This would measure the angle $\Delta\phi$ directly. The writer did not have a circle available to carry this out.

[1] Tool, PHYS. REV., XXXI., p. 1, 1910.

[2] Tuckerman, Univ. of Nebr. Studies, IX., No. 2, 1909.

The results of the observations are presented in Fig. 6, curve *A*. The ordinates give the rotation in degrees of the α and β axes in their plane per volt per centimeter normal to them. The fields used were about 8,000 volts per centimeter. The rotation reverses with the direction of the field and bears a right-hand screw relation to the directions of the lines of force. Referring to equation (16) the constant e_{41} was found to have the values:

$$-1.94 \times 10^{-8} \text{ at } 20^\circ \text{ C.},$$
$$-2.66 \times 10^{-8} \text{ at } 25^\circ \text{ C.},$$
$$-2.76 \times 10^{-8} \text{ at } 30^\circ \text{ C.}$$

In computing these, the fields were put in electro-static units and the values of the dielectric constant used were those determined by the writer and are plotted in Fig. 6, curve *C*.

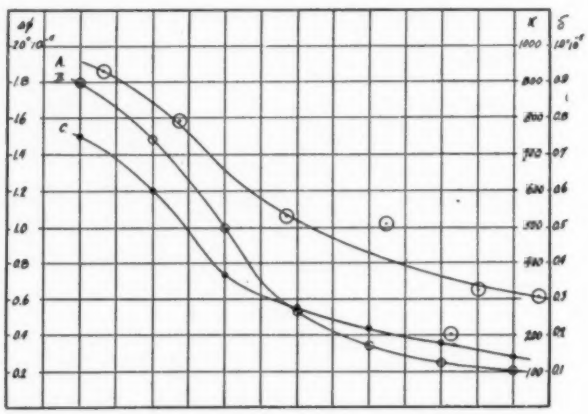


Fig. 6.

There is a decided decrease in the angular rotation as the temperature changes from 20 to 30° C. and the field is kept constant. To show the variation in piezo-electric modulus and dielectric constant in the same range, curves *B* and *C* are drawn. A comparison with curve *A* shows that the decrease in electric-optic rotation is less than that of either the piezo-electric modulus or the dielectric constant, although it is more nearly equivalent to the latter. Indeed, one observes that e_{41}, which refers to the rotation per unit polarization, increases continuously throughout this range.

This is a very striking result in view of the fact that the piezo-electric modulus decreases so appreciably. If the elastic coefficients and the piezo-optic constants do not change then the portion of the electro-optic effect due to electric deformation decreases in the same manner as the

piezo-electric moduli. The direct effect of the field on the vibrations of the dispersion charges would then necessarily increase and soon give nearly the whole effect. As this is improbable, it seems that there is a decided change in the elasticity or the piezo-optic coefficients or both. In the absence of definite data on these quantities no more can be said at present. The writer inclines to the view that an increase in elastic constants occurs sufficient to account for both the variation in the piezo-electric moduli and the increase in the electro-optic effect.

Pyro-electric Effect.

Although Rochelle salt is classed as a type of crystal that should give no pyro-electric effect, still the existence of a measurable polarization in the ă direction makes it possible that such an effect can be observed. The greatest difficulty in measuring it is the danger of exciting a piezo-electric effect due to non-uniform heating. Customarily, the charges which appear on the faces of the crystal are measured between two steady temperatures so that these errors tend to cancel out. Due to the difficulty of producing liquid insulating baths of steady temperature in the range to be investigated and because of the likelihood of leakage, a slow rate of heating was employed. The utmost precautions were taken to keep the heating uniform. The crystal plate was made circular so that the residual thermo-elastic stresses would have a symmetrical distribution and balance their piezo-electric action. This plate was suspended by the leads inside two concentric cylinders of brass. Copper diaphragms and plugs of wool in the ends served to make the temperature distribution uniform. To test the symmetry of the heating, measurements were made with the crystal in two positions at 90° to each other so as to give the complementary distribution of stresses. This just reversed the error due to the piezo-electric effect.

The charge was measured as it appeared on the faces, beginning at − 70° C., by an electrometer compensating system. This always kept the faces of the crystal nearly at zero potential and eliminated leakage to a large extent. In Fig. 7 several curves are shown which give as ordinates, the pyro-electric charge developed between − 70° C. and the temperature plotted as abscissa. Curve *C* gives the results obtained with the crystal rotated 90° to its previous position.

Attention is rather called to the general nature of these curves than to numerical values although it may be noted that the electrode area was 1.44 cm.^{2} The piezo-electric error has been largely eliminated for it will be observed that the results were very similar in the complementary positions mentioned above. In addition to this, the variation with

temperature does not approach the magnitude of that shown by the piezo-electric charge for constant stress. The heating rate was constant and this should have made the stresses nearly constant. These facts all point to the pyro-electric character of the charge measured.

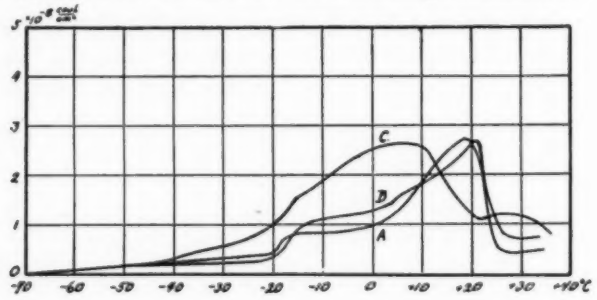


Fig. 7.

Since the dilatation of the crystal varies uniformly, this charge cannot be accounted for by expansion and it is therefore what is termed a "real" pyro-electric effect. The pyro-electric coefficient or change in surface density of charge, which is proportional to the derivative of the curves shown, evidently reverses sign just below room temperature and becomes very large. The existence of a real pyro-electric effect is of special interest because of its apparent non-existence from data obtained on other crystals.[1] It may be advisable to make a quantitative determination by some accurate method.

NEUMANN'S PRINCIPLE.

In the case of Rochelle salt the mere existence of any kind of polar effect is of great interest because of the symmetry of the crystal form. Rochelle salt is always classified as a hemihedral orthorhombic crystal. It does not have any polar symmetry in its crystal form and hence should have no directed physical properties. This conclusion is based on Neumann's principle[2] which is a very fundamental hypothesis in crystal physics. It states that the physical properties have always at least the symmetry of the crystal form. Applications of this principle are extensively used to reduce general physical formulæ to their simplest form for any particular type of crystal form.

If Rochelle salt is really in the hemihedral class of the orthorhombic system, then much of the data collected by the writer and others disprove the exactness of Neumann's principle. There are various effects so far studied that show a definite polarity in the ă crystallographic direction. In the first place there are the condenser charge and discharge throws

[1] Lindemann, Ann. d. Phys., 62, No. 2, 107, 1920.

[2] Voigt, Krystallphysik, p. 3 and p. 20.

which Anderson[1] first showed were different in the two directions, together with the unsymmetrical hysteresis loops that grew out of the writer's[2] study of Anderson's experiments. Secondly, the piezo-electric property in various electric fields shows a decided dependence on the direction of the field. Then there is also the unidirectional conductivity at some temperatures, and finally there is good evidence for the existence of a pyroelectric effect. This proves conclusively that Rochelle salt has directed electrical properties in the ă direction.

It may be that a careful study of the crystal form will show that it is not hemihedral but possibly hemimorphic and thus save Neumann's principle. All of the work done by the writer has been on material furnished by two large crystals presented by Dr. W. R. Whitney of the General Electric Company. A record of a rough crystallographic examination of the first one to be used up did not contain any reference to a polar structure. The second crystal, examined more recently, does show something that points in this direction and was not noticed at first. A drawing of the base of the crystal is shown in Fig. 1*B*. The faces indicated are all prism faces, no pyramids being present, the ends of the c axis being bounded by pinacoids. The sphenoidal faces were not present. It will be observed that the ă direction has on one side a very narrow face normal to the axis, while the other side is bounded by sloping planes. In other respects the planes occur in closed groups unless one considers the few irregularities in flatness on some of the broader faces.

If Rochelle salt is hemimorphic much of the work done on its properties will be incomplete, since all of the coefficients pertaining to any physical property would not be known. To find these would necessitate measurements in several other known directions suitably chosen with respect to the crystallographic axes. The complete set of coefficients would then appear as solutions of a set of simultaneous linear equations. The number and character of the coefficients to be determined will depend on the symmetry of the physical agency and the reaction to which it is related. These are classed by Voigt[3] as scalars, *e.g.*, temperature; vectors, *e.g.*, fields; and tensor tripels, *e.g.*, stresses or strains. Thus piezo-electric phenomena consist of relations between a tensor tripel, stress, and a vector, electric polarization. This type of relation requires in general eighteen coefficients for its complete specification. The three components of polarization are expressed by Voigt as linear functions of the six stress components as follows:

$$P_x = \delta_{11}X_x + \delta_{12}Y_y + \delta_{13}Z_z + \delta_{14}Y_z + \delta_{15}Z_x + \delta_{16}X_y, \quad \text{etc.}$$

[1] Anderson, Report to the National Research Council, Mar. and Apr., 1918.
[2] Valasek, PHYS. REV., XVII., p. 475, and XIX., p. 478.
[3] Voigt, Krystallphysik, p. 122.

In the orthorhombic system the piezo-electric moduli are reduced by Neumann's principle to the following sets:

I. Hemimorphic Group (A_x^2, E_x)

0	0	0	0	δ_{15}	0
0	0	0	δ_{24}	0	0
δ_{31}	δ_{32}	δ_{33}	0	0	δ_{36}

II. Hemihedral Group (A_x^2, A_x^2)

0	0	0	δ_{14}	0	0
0	0	0	0	δ_{25}	0
0	0	0	0	0	δ_{36}

This brings up a consideration that places another aspect on the situation. A plate normal to the ă axis will give, in the first system above, a charge *only* when subjected to a Z_x shear. Measurements made on a plate so oriented show under a Y_x shear, the large piezo-electric effect characteristic of Rochelle salt. This seems to prove that Rochelle salt belongs to the hemihedral group since these results are in keeping with the nature of the second system of moduli given above and not in agreement with the first.

This contradictory array of facts is very puzzling, for their validity cannot be doubted. Perhaps, after all, Neumann's principle is only approximately true or probably not as general as it has been supposed to be. One may say that the crystal is made more or less polar by the physical agency applied, but this is only another way of saying that Neumann's principle is not exact or that it holds only in the limit when the stresses or fields are very small.

PIEZO-ELECTRIC THEORY.

There have been several explanations proposed for the piezo- and pyroelectric phenomena. In order to account for pyroelectricity, Lord Kelvin[1] assumed the elements of the crystal structure to be permanently polarized. Under ordinary conditions surface charges compensate for their induction at external points, but when the temperature changes the moment alters, and free charges appear on certain faces. Riecke[2] generalized this idea to account for piezo-electric phenomena as well. His "crystal molecules" consisted of rigid pole systems of specified form instead of a simple dipole. A compression or temperature change would alter the distance between them and thus change the moment and cause the appearance of charges.

[1] W. Thomson, Phil. Mag. (5), 5, p. 26, 1878.

[2] Riecke, Nach. Ges. d. Wiss. Gott., 1891.

Later Voigt [1] modified Riecke's theory by assuming that the pole systems could be distorted. One advantage of this view is that a permanent polarization is made unnecessary. This is in better harmony with experiment. Phenomena which would accompany a high surface density of charge demanded by Riecke's theory have never been observed. Moreover, Voigt showed that the permanent polarization in tourmaline is small and equal to the pyro-electric response for a change in temperature of only 26° C. Thus he found that the permanent polarization became zero if the crystal was heated to 50° C. The writer[2] has measured the permanent polarization of Rochelle salt in the ă direction and also found that it is of the order of magnitude of variations in it. It is equal to the piezo-electric excitation for one hundred grams or equal to the polarization produced by a field of only 15 volts per centimeter. Applied fields of between -1600 and $+1600$ volts per centimeter decidedly change and even reverse the direction of this polarization while they do not reverse the piezo-electric response at all. They merely change its value in such a way that it approaches zero for large fields of either sign. This shows that the changes in polarization represented by the piezo- and pyroelectric effects are not dependent on the existence of a permanent polarization.

An explanation based on different assumptions was first made by the Curie brothers[3] and developed later by Lord Kelvin.[4] The basic idea is that the crystal molecules consist of connected dissimilar parts having definite contact differences of potential. Any orderly arrangement of such rigid crystal elements connected by quasi-elastic forces acting like elastic non-conducting springs, will take on a definite charge distribution due to the contact differences of potential and depending in amount on the capacities between the various parts.

A distortion of such an arrangement will change the capacities and cause changes in the potentials of insulated plates on the faces of the crystal. Lord Kelvin points out in detail how such a mechanical model can be made to give any desired value to the twenty-one piezo- and pyroelectric coefficients and satisfy any type of crystal. A real pyro-electric effect may also be produced in this model by the distortion of certain springs by the temperature, so that even if the faces are fixed, the inner molecules rotate.

On either Riecke's or Lord Kelvin's theory, a varying piezo-electric effect such as occurs in Rochelle salt at certain temperatures would

[1] Voigt, Nach. Ges. d. Wiss. Gott., 1893.
[2] Valasek, PHYS. REV., XVII., p. 480.
[3] J. and P. Curie, C. R., *92*, 352, 1881.
[4] W. Thomson, Phil. Mag. (5), *36*, 453, 1893.

arise from a change in either the crystal structure or the forces between crystal elements. Circumstances tending to alter the grouping of these elements are known to have pronounced effects on the piezo-electric property, but such alterations in the structure in the two critical temperature ranges of Rochelle salt do not occur. For example, between -20 and $-30°$ C., the piezo-electric activity decreases a thousand fold with no noticeable variation in heat absorption, dilatation, or refraction. These surely would change if the crystal form were altered.

The alternative is to suppose that the forces between crystal elements change at these temperatures. These forces are related to the cohesive forces and the elastic constants. They may vary either by changing the distances between the crystal elements or by changing their structure and hence their external field. A change in molecular structure likewise appears a little doubtful because of the constancy of the specific rotatory power. Probably this and other optical properties give no information on the piezo-electric structure because it does not involve charges with frequencies near the visible region. It appears that transformations in large ions or groups, and changes in the elastic properties of Rochelle salt occur to account for the variations in the piezo-electric activity, since these could not have been detected by the methods employed. The elastic constants await study.

If the x-ray analysis were not so difficult for this type of crystalline organic compound, it would be worth while to study the crystal structure and reflection coefficients by this means. The writer thinks that some of his previous work shows that the piezo-electric structure is intimately bound up with the water of crystallization. The place this occupies in the crystal structure and in crystal formation in general is therefore of great interest.

The writer expresses his gratitude to the National Research Council for the grant of a fellowship which enabled him to pursue this work.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
July, 1922.

LOW VOLTAGE ARCS IN DIATOMIC GASES.

I. HYDROGEN, NITROGEN, AND IODINE.

BY O. S. DUFFENDACK.

SYNOPSIS.

Low-voltage Arcs in Hydrogen, Nitrogen, and Iodine Vapor.—After a general review of the previous experimental results and theoretical suggestions, (1) *current-voltage curves* obtained with a simple two-electrode tube are described. Precautions were taken to insure pure gases. The breaking potential was always the ionizing potential of the gas, 16.3, 16.2, and 14.6 volts, respectively, for the three gases. The striking potential was greater than the breaking one by an amount which increased with the pressure and with increasing cathode filament temperature. *In dissociated hydrogen*, maintained at a high temperature within a thin tungsten cylinder heated electrically, an arc was readily maintained at the ionizing potential of the atom, 13.7 volts, and under very favorable conditions, at the radiating potential, 10.0 volts. *In dissociated iodine vapor*, the arc was maintained at 12.1 volts and under certain conditions at the ionizing potential, 10.2 volts. Nitrogen was not appreciably dissociated in the furnace. *The critical potentials* given above agree with the best previous results within ± 0.2 volt as a rule. Those associated with the atom are experimentally distinguished from those associated with the molecule.

Electric Furnace Spectra of Hydrogen, Nitrogen and Iodine to 2500° C.—In hydrogen, the series lines flashed in when the arc was struck, even as low as 10.6 volts, but the bands did not appear. Evidently the series lines are due to the atom and the bands to the molecule. In nitrogen, a brilliant "flare" was produced at potentials which decreased from 70 to 40 volts as the temperature was increased. This "flare" shows both the positive and negative bands along with the spectrum of tungsten; it is probably due to the formation of "active" nitrogen. At 70 volts the first lines, 5006 and 5003 Å., appeared, and at 90 volts only two more, 5680 and 5667 Å. Reasons are given for assigning the positive bands to the neutral molecule, the negative bands to the ionized molecule and the lines to the atom. In iodine, the arc lines, particularly 4860 Å., flashed in when the arc struck, the enhanced lines coming in at higher voltages. No band spectrum appeared.

New negative bands of nitrogen were found at 5075, 5018 and 4961 Å.

GENERAL THEORY OF LOW VOLTAGE ARCS.

THIS investigation was undertaken to see if additional light could be obtained by this method upon the critical potentials of diatomic gases; to study the effect of the dissociation of a gas upon the potentials at which an arc will strike and break; and to investigate, incidentally, the excitation of the spectra of the substances.

The method of investigating critical potentials by means of low voltage arcs differs from the methods usually employed for determining ionizing and radiating potentials in that very much greater electron

streams are passed through the gas and the gas is usually at a considerably greater pressure. Up to the time this investigation was begun this method had been employed only with monatomic gases and vapors. Some seeming disagreements appeared between the results obtained by means of low voltage arcs and those by the usual methods. When only a moderately dense electron stream was sent through a gas, the arc would strike at the ionizing potential as determined by the usual methods, but when a dense electron stream was employed the arc could be made to strike as low as the radiating potential. The striking of an arc indicates that considerable ionization is taking place, and this is confirmed by the appearance of the spectrum of the substance. As Bohr's theory indicates that the atom is not ionized at the radiating potential, and as the usual methods often indicate the absence of ionization, the striking of the arc at this potential appeared to be in conflict with the previous results.

Various explanations of these anomalous effects with dense electron streams have been proposed. In some cases it was thought that the ionization of impurities present might account for the effect, and McLennan[1] attributed the appearance of "faint arcs" to electrons of abnormally high velocities in the electron stream. These explanations seemed insufficient in most cases and others were proposed. Millikan[2] suggested that the radiation produced by impacts at the radiating potential might act photoelectrically upon the atoms of the filament or of the gas and thus produce additional electrons which would in turn be accelerated by the applied field and make impacts at the radiating potential and so there would be a multiplication of the original current. Richardson and Bazzoni[3] and Van der Bijl[4] put forward the theory of successive impacts, and the former also suggested that a combined action of radiation and of impacts accounts for the ionization. K. T. Compton[5] investigated the adequacy of the theory of successive impacts and concluded that, while it is an important factor, in general, ionization produced in this way is insufficient to account for the observed results. He has recently shown[6] that the cumulative effect of absorbed radiation is far more effective than successive impacts, and it seems that this may account for most of the cases reported.

In order to understand better the results obtained, it will be well for

[1] Proc. London Phys. Soc., 31, 1 (1918).
[2] PHYSICAL REVIEW, 9, 378 (1917).
[3] Nature, 48, 5 (1916).
[4] PHYS. REV., 10, 546 (1917).
[5] PHYS. REV., 15, 130, 476 (1920).
[6] Amer. Phys. Soc. Proc., New York meeting, 1922.

us to recall what is meant by an arc. Richardson has shown that the saturation thermionic current from an incandescent cathode is given by

$$i = aT^2\epsilon^{-\frac{b}{T}}$$

where a and b are constants and T is the absolute temperature of the filament. When this equation is tested, however, it is found that, while it holds quite well at the lower temperatures, the current falls short of the value predicted by the equation for the higher temperatures and reaches a maximum value which is much less than the saturation current. The point of departure from the Richardson relation depends upon the voltage applied and is earlier for the lower voltages. The maximum current obtainable is likewise less the lower the voltage.

The reason for the failure of Richardson's equation was investigated by Langmuir,[1] and it was found to be due to the effect of the space charge of the emitted electrons. If no electrons are emitted by the filament, the potential will vary linearly between the electrodes. When electrons are emitted and, under the influence of the field, pass over to the anode, they form an electric current and build up a space charge. The potential gradient will no longer be uniform between the electrodes but will be less near the filament on account of the concentration of electrons there. These electrons will repel one another and so will impede those just being emitted by the filament. As the speed of an electron is proportional to the potential gradient, there will be a diminution of the average velocities of the electrons near the filament and a resulting increase in concentration. This results in increased impedance until finally the space charge becomes so great that the potential gradient becomes zero or even negative. An equilibrium condition will be reached in which the electrons emitted with velocity components parallel to the electric intensity below a certain amount will be stopped and driven back to the filament. There can then be no further increase in current at the prevailing temperature of filament and potential applied.

Now if ionization takes place, we have a quite different state of affairs. The positive ions will neutralize the space charge of the electrons. The densities of electrons and of ions, and hence the space charges due to them, will vary inversely with their velocities. Their velocities vary directly as their mean free paths and inversely as the square roots of their respective masses. Thus each positive ion neutralizes the space charge of $4\sqrt{2}\sqrt{1846\,M}$ electrons, where M is the molecular weight.[2] Therefore,

[1] PHYS. REV., 2, 543 (1913).

[2] The factor 4 is due to the negligible size of the electron and the factor $\sqrt{2}$ to the fact that its speed is of a higher order than that of the molecules among which it moves. See any treatise on Kinetic Theory.

one positively charged hydrogen atom will neutralize the space charge of 243 electrons, one positively charged hydrogen molecule will neutralize 343 electrons. Now if we have reached the maximum current limited by the space charge, the formation of one positive hydrogen molecule ion will permit the emission of 342 additional electrons. If every electron emitted ionized a molecule, the electron current would increase more than three hundred times. These newly emitted electrons would in their turn be accelerated and would ionize other molecules, and so on, and the current would continue to increase until the saturation current indicated by Richardson's equation is reached. To this current would be added the current carried by the ions and electrons formed in the process of ionization. There would be a further increase in emission due to the heating of the filament as a result of its bombardment by positive ions, and there would be a diminution of current due to the recombination of ions and electrons. The data from hydrogen show ratios of current in the arc to that before the arc of from 2 to 120 depending upon the temperature of the filament. The current through the arc was about that to be expected from Richardson's equation.

Now let us look a little further into the mechanism of the arc. When the space charge immediately surrounding the filament is neutralized or reversed by positive ions, we will have a large increase in electron emission from the filament, and the arc will strike. This is accompanied by a redistribution of the electric intensity in the tube, resulting in a large drop in potential near the cathode. This fall in potential will be a large fraction of the total potential difference between the electrodes, but, obviously, the potential can nowhere be higher than at the anode as this would give a negative gradient and would prevent electrons which had lost their velocities from reaching the anode. The exact distribution of potential cannot be computed for want of knowledge concerning the distribution of space charges. This cathode fall of potential will enable electrons to ionize at their first impact, or, at least, it will greatly increase the ionization near the cathode. This view of the distribution of electric intensity in the arc is supported by the observations that the spectrum is most intense in the region near the filament and that the glow of the arc, if it is small, is confined to the region immediately surrounding the filament.

If we assume the distribution of electric intensity explained in the preceding paragraph, the potentials at which an arc will strike and break can easily be deduced. As the striking of the arc follows the neutralization of the space charge, it will normally occur at or above the ionizing potential of the substance, depending upon the temperature of the

filament and the pressure of the gas. If a considerable fraction of the molecules are in a partially ionized condition, due to the absorption of a quantum of radiation or to an impact with an electron possessing sufficient energy to displace an electron in the molecule but not to remove it, a sufficient number of positive ions may be formed by impacts with these molecules to cause the arc to strike at a potential below the ionizing potential. As it seems improbable from Professor Compton's[1] work that this can be accomplished by successive impacts alone, we need examine only the case of the absorption of radiation. If, as is usually the case, the radiation comes from the substance itself and not from without, electron impacts at the radiating potential will be required to produce the radiation, as radiation corresponding to the first line of the principal series is necessary. Therefore, it is possible to get an arc to strike at a potential equal to the difference between the ionizing and radiating potentials of the substance, provided that this difference is not less than the radiating potential; or at the radiating potential, provided that this is not less than half the ionizing potential. With dense electron streams, the arc has been made to strike in all of the monatomic gases thus far investigated at the radiating potential. It is noteworthy, however, that a distinct time lag in the striking of the arc was noted by nearly all of the observers for voltages between the radiating and ionizing potentials. It was found impossible to get the arc to strike in the diatomic gases investigated at a voltage less than the ionizing potential. This is probably due to the loss of energy by inelastic impacts in the diatomic gases and to the fact that the molecules are unable to absorb and reëmit the resonance radiation, which comes from the atoms.

After the arc has struck, it will continue as long as the space charge surrounding the filament remains positive. With a dense electron stream the arc can be maintained indefinitely at the radiating potential in a monatomic gas, provided that this is not less than half the ionizing potential. Obviously, the arc can be maintained temporarily at a voltage equal to the difference between the ionizing and radiating potentials even when this is less than the radiating potential, but it must eventually break due to the loss of radiation from the tube.

In diatomic gases the arc invariably broke at the ionizing potential, but it is comparatively easy to maintain the arc in monatomic gases at the radiating potential when this is not less than half the ionizing potential. In some cases the arc has been maintained for a considerable time at the radiating potential, or less, even when this is less than half the ionizing potential. This was done in the case of mercury vapor by Hebb,[2]

[1] Loc. cit.

[2] PHYS. REV., 9, 371 (1917); 12, 482 (1918).

Millikan,[1] and Compton and Yao;[2] in sodium vapor by Wood and Okano,[3] and in mixtures of sodium and mercury and potassium and mercury vapors by Hebb. That these are not anomalous cases was shown by Compton and Yao, who worked out a satisfactory explanation of these cases upon the basis of the distribution of velocities of emission of the electrons. The ionizing potential of mercury is 10.4 volts and the radiating potential is 4.9 volts. Compton and Yao maintained the arc in mercury vapor at 1.8 volts. They showed that there are a sufficient number of electrons emitted from a hot filament with initial velocities sufficient to make up the difference between the 1.8 volts observed and the 5.5 volts theoretically required to maintain the arc.

The case of helium is a more striking one. The ionizing potential of helium is 25.5 volts and radiating potentials of 20.4 and 21.2 volts have been found. It should, therefore, be possible to maintain an arc in helium temporarily at 5.1 or 4.3 volts. Kannenstine[4] got evidence that this can be done by taking oscillograph records of the current through a helium arc when an alternating field is applied. These records show a persistence of the arc at about 4 volts when a sixty-cycle circuit was used. This would give a time interval of the order of a hundredth of a second. Compton, Olmstead, and Lilly,[5] maintained an arc for a considerable time at 8 volts, and Miss Davies's [6] work indicates that the arc can be maintained for an indefinite period at 13 volts. These observers do not claim that these voltages are critical potentials; the important point is that in the case of helium it seems possible to maintain an arc indefinitely at a potential far too much below the radiating potential to allow an explanation on the basis of velocity distribution. Miss Davies suggest that helium is converted into a metastable form by electron impacts at 20.4 volts and that this is then ionized by impacts of 5.1 volts or more. When these ions are neutralized the atom remains in the metastable condition and does not return to the normal form. Once this is formed, then, the arc can be maintained at a potential as low as 5.1 volts until the helium is reconverted into the normal form. The process by which the metastable atom is changed into the normal atom is not well understood, although Franck and Knipping[7] suggest that it depends upon the catalytic action of impurities. It should be noted that the arc does not strike in helium at potentials less than 20.4 volts.

[1] PHYS. REV., 9, 378 (1917).
[2] Amer. Phys. Soc. Proc., Washington meeting, 1922.
[3] Phil. Mag., 34, 177 (1917).
[4] Amer. Phys. Soc. Proc., New York and Washington meetings, 1922.
[5] PHYS. REV., 15, 545 (1920).
[6] Roy. Soc. Proc., A, 100, 599 (1922).
[7] Zeit. für Physik, 1, 320 (1920).

APPARATUS.

The apparatus employed in this investigation was of two types. The first was a simple two-element tube, consisting of a tungsten wire filament and a nickel plate anode placed at a distance of about 5 mm. from the filament. A potential difference was applied between the negative end of the filament and the plate and could be varied by control rheostats. The current between the electrodes was read on a sensitive milliammeter placed in series with the arc. The current through the arc was recorded as the voltage was raised by steps from zero. The striking of the arc was indicated by a sudden jump in the current and also usually by the appearance of a glow around the filament and the flashing in of the spectrum of the gas. The potential across the arc was corrected to that which obtained between the middle of the filament and the plate by subtracting from the reading of the voltmeter half the potential drop across the filament. This correction is subject to error when the filament is very hot as there may then be sufficient emission from the negative end of the filament to maintain the arc. The effect of initial velocities of emission from the filament is such as to more or less counterbalance this error.

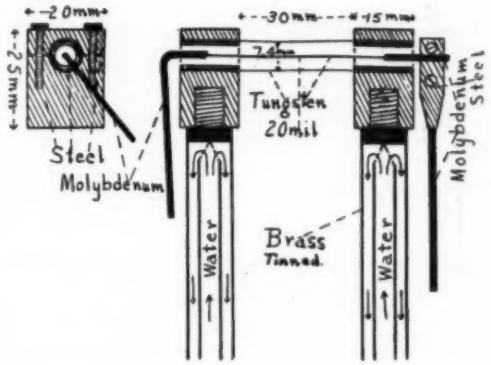


Fig. 1.

It was found impossible in the simple tube to maintain the arc at voltages less than the ionizing potential. The failure to do so was ascribed to there being an insufficient amount of the monatomic gas present in the tube when due only to the dissociating action of the filament and of the arc. Professor Compton suggested that it might be possible to dissociate hydrogen and other gases by means of a tungsten furnace which could also be used as one of the electrodes of the arc. The construction of the furnace developed by the writer is shown in the accompanying diagram. It consists of a cylinder of very thin sheet tungsten mounted on water cooled leads. A tungsten filament ran

axially through the cylinder and was made the cathode. The fall of potential in the furnace and that in the filament were in the same direction. In the earlier experiments with this tube, the potential was applied between the positive end of the furnace and the negative end of the filament. The reading of the voltmeter was corrected to give the potential between the middle of the electrodes by subtracting half the sum of the voltage drops across the furnace and the filament. This correction was checked by a sharp rise in the thermionic current when the voltmeter read this amount. This correction is subject to the same error as in the case of the simple tube for very hot filaments. The parts of the furnace were later modified so that the drops of potential in the furnace and in the filament and also in the furnace leads and filament leads were identical. The potential was then applied between the negative ends of the furnace and filament and the voltmeter read the voltage obtaining between corresponding parts of the furnace and the filament.

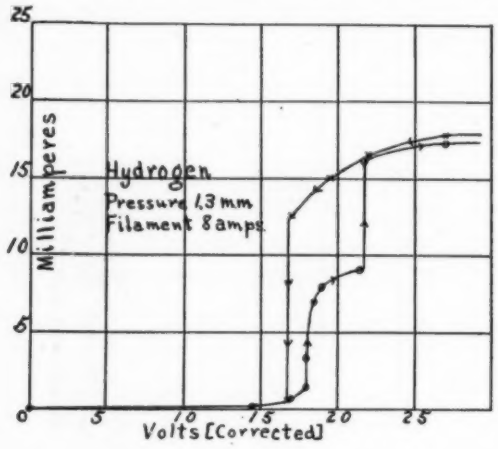


Fig. 2.

This condition was practically equivalent to having two equipotential surfaces as electrodes. The temperature of the furnace was estimated from the resistivity of the tungsten. Calculations of the resistivity showed that temperatures of about 2,500° C. were obtained.

ARCS IN HYDROGEN.

The hydrogen was generated by the electrolysis of dilute sulphuric acid and was purified by passing it over phosphorous pentoxide and through charcoal immersed in liquid air. The pressure of the gas in the tube was read on a McLeod gauge. Before the gas was admitted into the tube, the electrodes were thoroughly glowed out, and when the simple tube was used, it was thoroughly baked.

Figs. 2, 3, and 4 show the effect of the temperature of the filament on the potential at which the arc strikes and breaks. These curves were obtained from three successive runs in hydrogen at a pressure of 1.3 mm. The potential of the break is lower the greater the filament current, becoming slightly less, Fig. 4, than the ionizing potential of hydrogen. This illustrates the error in the zero correction for hot filaments as pointed out in a foregoing paragraph.

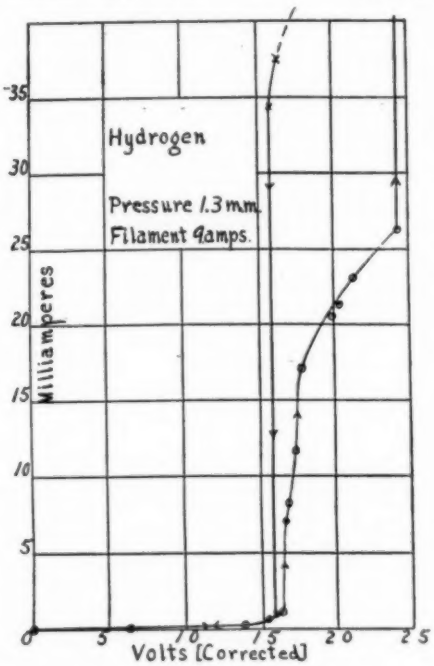


Fig. 3.

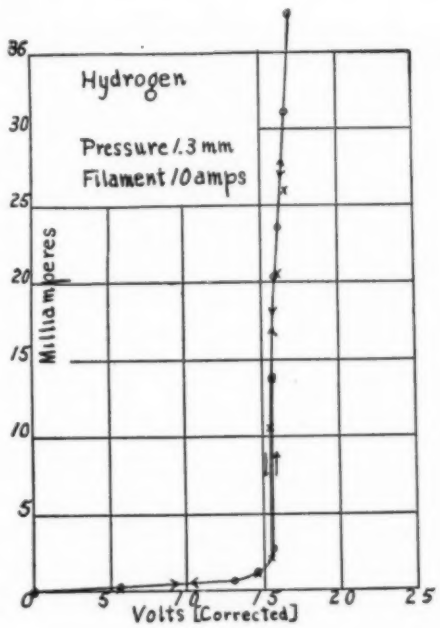


Fig. 4.

Figs. 5, 6, and 7 show the effect of the pressure of the gas upon the potentials at which the arc strikes and breaks. For these curves runs were taken at pressures of 0.4, 2.4 and 5.5 mm. and the filament currents were such as to give practically the same increase in current when the arc struck. The striking potential regularly increases with the pressure as does the difference between the striking and breaking potentials. The curves indicate that there is an optimum pressure at which the arc can be maintained to the ionizing potential of the gas with a moderately hot filament.

At pressures above about 0.5 mm. ionization sets in at the ionizing potential as is indicated in Figs. 2, 3, 6 and 7, but, though there may be a large increase in current, the arc does not strike until the voltage is raised considerably above the ionizing potential, the amount depending

upon the pressure of the gas and the temperature of the filament. If the applied potential is decreased before the arc strikes, the curve is retraced, but after the arc strikes, the current remains at a higher value until the

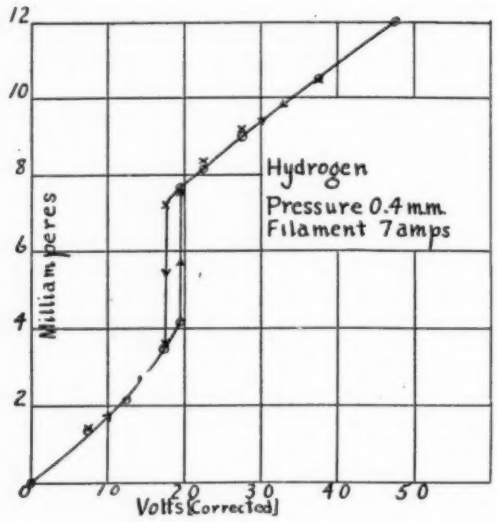


Fig. 5.

arc breaks. Before the arc strikes, the current seems to approach a saturation value as in the case of thermionic currents in high vacua. This is probably due to a gradual shifting of the region of predominately positive space charge toward the filament. A large fraction of the potential difference applied to the electrodes is used up between the filament and the boundary of the region of positive space charge, and so the electrons enter this region at approximately their maximum speeds, the actual speed depending upon the potential and upon energy losses by inelastic impacts. The energy losses by inelastic impacts are greater for the higher pressures due to the increased number of collisions, and so the potential difference required to be applied to cause an electron to enter the region of positive space charge with sufficient energy to ionize upon impact will be greater the greater the pressure of the gas. This accounts for the increase in the striking potential with the pressure. Now, after this region of positive space charge has reached a certain thickness, a further increase in thickness will not greatly increase the probability that an electron entering this region with energy sufficient to ionize a molecule will make an ionizing impact. There will then be very little increase in current until the space charge immediately surrounding the filament becomes positive, and the arc strikes. After the

apparent saturation current has been reached, a slight change in the conditions in the tube or a slight shifting of the space charges will cause the arc to strike, and so the striking of the arc may vary by several volts for the same pressure and filament current.

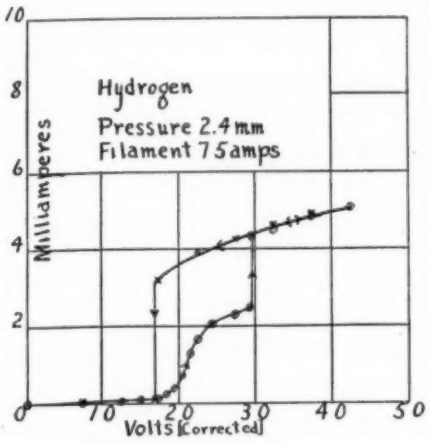


Fig. 6.

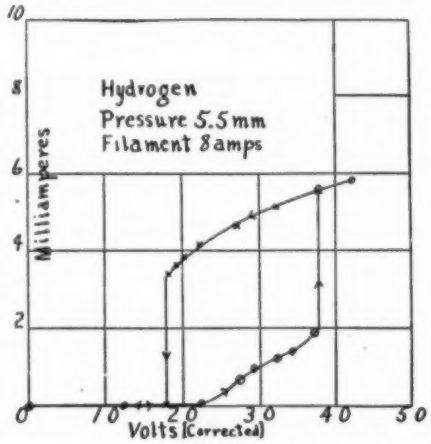


Fig. 7.

In this type of apparatus the potential of the break of the arc was far more constant than that of the strike. For pressures between 0.85 mm. and 3 mm. and with moderately hot filaments the breaks were remarkably constant, having a mean deviation from the average of 0.3 volt. The average of fourteen runs at these pressures gives a breaking potential of 16.35 volts which is within the range of the values of the ionizing potential of hydrogen reported by various observers.

As Bohr's theory puts the ionization potential of the hydrogen atom at 13.52 volts, calculated from the convergence frequency of the Lyman series, and the radiating potential at 10.14 volts, it should be possible to maintain the arc at these potentials if a sufficient amount of monatomic hydrogen could be obtained. The tungsten furnace was designed to dissociate the gas by means of high temperatures. The amount of dissociation to be expected was calculated by means of Nernst's equation of the "reaction-isobar,"

$$\log \frac{x^2}{1-x} P = -\frac{Q_0}{4.571\,T} + 1.75 \log T - \frac{\beta}{4.571} T + \sum \nu C.$$

x = the fraction of the molecules present which are monatomic,
P = the total pressure,
Q_0 = the heat of dissociation at absolute zero,
T = the absolute temperature,
β is a constant depending upon the rate of change of the specific heat with the temperature,

4.571 is the gas constant per gram mol. times the logarithmic modulus,

C is Nernst's chemical constant.

Q_0 can be calculated from Q, the heat of dissociation at ordinary temperatures, by means of the formula: $Q=Q_0+\alpha T+\beta T^2+$ etc., where α = specific heat.

Taking the heat of dissociation, Q, to be 84,000 calories per gram-molecule, $\beta = 0.000225$, and the chemical constants for diatomic and monatomic hydrogen to be[1] -3.4 and -1.6 respectively, the percentages of monatomic hydrogen in equilibrium with diatomic hydrogen at various temperatures and pressures are indicated in the following table:

Pressure.	1000° K.	1500° K.	2000° K.	2500° K.	3000° K.
0.5 mm.....	.005	2.36	61.5	Complete	
1.0 mm.....	.004	1.69	49.5	98.8	
5.0 mm.....	.002	0.74	26.7	90.4	Dissociation

When the furnace was not heated, the arc struck and broke at the ionizing potential of the molecule, and there was no evidence of ionization below about 16 volts. With the furnace hot, considerable ionization was produced at about 10 volts and 13.5 volts as is indicated by the

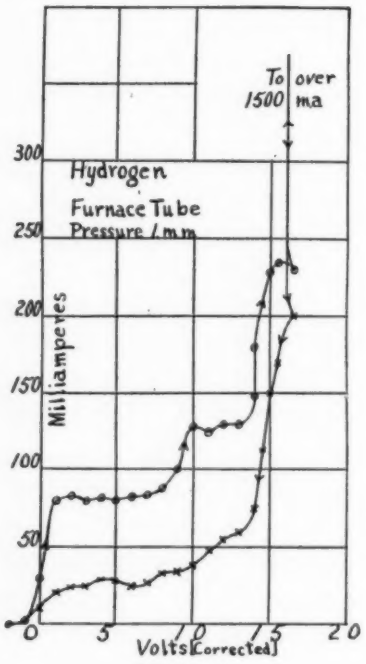


Fig. 8.

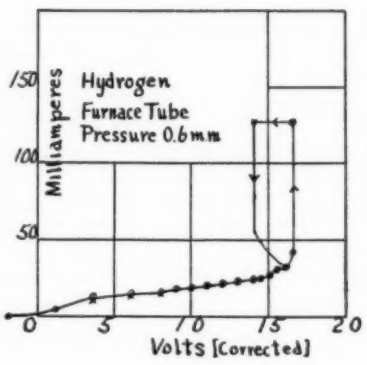


Fig. 9.

[1] Reiche, Ann. d Physik, 58, p. 657, 1919 and Schames, Phys. Zeit., 21, p. 41, 1920.

curve for the thermionic current, Fig. 8. Later a temperature was reached at which the arc struck at the ionizing potential of the molecule and was maintained to the ionizing potential of the atom, Fig. 9, indicating that the increase in dissociation in the arc enabled it to be maintained in monatomic hydrogen. Finally, practically complete dissociation was obtained; the arc struck easily at the ionizing potential of the atom, and the curve shows no indication of a further increase in ionization at the ionizing potential of the molecule, Fig. 10(*b*). With a very hot furnace and a large electron emission the arc was made to strike at 10.6 volts, Fig. 10(*a*) which is very near the radiating potential of the atom, and no further discontinuities were observed at higher voltages. It was quite difficult to do this and it was only done when the furnace had not been maintained at the high temperature for a long time. The curve 10(*a*) was drawn from memory. This striking of the arc was repeated several times and the potential and current noted, but an accident prevented a run being made with the current and voltage recorded by steps. The failure to get the arc to strike at potentials lower than 13.5 volts later was attributed to impurities coming from the walls of the tube and from the clamps and leads when they became warm. As the furnace was mounted on water-cooled leads, the tube had to be put together with Khotinsky cement and so it could not be baked out.

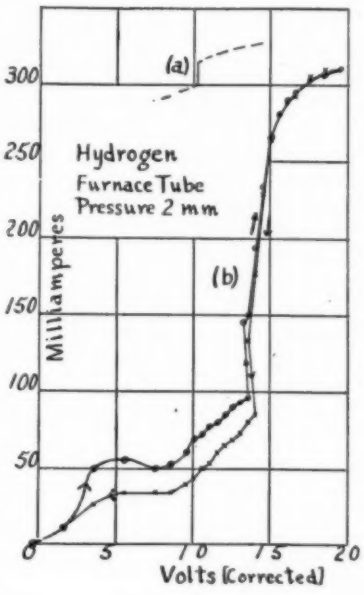


Fig. 10.

This is the first experiment of this kind performed in an atmosphere of atomic hydrogen, and these results constitute, it is believed, the first direct experimental proof of the correctness of the values of the radiating and ionizing potentials predicted by Bohr's theory for the *hydrogen atom* and of the interpretation of the ionizing potential of the molecule as due to its dissociation plus the ionization of one of the atoms.

Table I. gives the critical potentials of hydrogen predicted by Bohr's theory together with the average break points obtained in this investigation and the critical potentials reported by various observers. The heat of dissociation was calculated in each case by subtracting the thirteen-volt break from the sixteen-volt break when ionization was reported in

TABLE I.

Bohr's Theory.	This Investigation.	Franck, Knipping & Kruger.[1]	Davis & Goucher.	Horton & Davies.[3]	Compton & Olmstead.[4]	(Mohler & Foote)[5] Foote, Mohler & Kurth.[6]	Boucher.[7]
29.74 $D+2I$		30.45 $D+2I$					
26.36 $D+I+R$							
22.98 $D+2R$							
16.22 $D+I$	16.35 $D+I$	17.1 $D+I$	15.8 I	16.9 I 14.4 I	15.9 $D+I$	(16.5 I) 16.0 I	15.6 I
13.52 I	13.7 I	13.6 $D+R$	13.6 R	13.9 R	13.4 I	(13.3 I) (12.2 R)	13.6 I
12.84 $D+R$		11.5 I(Mol)				11.8 R 10.5 R	
10.14 R	10. R		11. R, I'	10.5 R	10.8 R, I'	(10.4 R) (3.2 D)	10.1 R
2.7 D	2.55 D	3.5 D		2.5 D	2.5 D	2.7 D	2.0 D

[1] Verhand. d Deutsch. Phys. Ges., 21, 728 (1919).
[2] PHYS. REV., 10, 101 (1917).
[3] Roy. Soc. Proc., A, 97, 23 (1920).
[4] PHYS. REV., 17, 45 (1921).
[5] Jour. Optical Soc. Amer., 4, 49 (1920).
Bureau Standards, 1920, 670.
[6] Amer. Phys. Soc. Proc., Toronto Meeting, Dec., 1921.
[7] PHYS. REV., 19, p. 189, 1922.

both cases. The heat of dissociation was measured by Langmuir[1] who found it to be equivalent to 3.6 volts.

It was not the purpose of this investigation to determine accurately the critical potentials of the gases studied, and no great degree of accuracy is claimed for the potentials reported. The purpose of this investigation was to interpret and not to determine critical potentials.

Spectroscopic Observations on Hydrogen.

A systematic study of the excitation of the spectrum of hydrogen was made during the investigation of the arcing characteristics. A Hilger direct-reading spectroscope was used and visual observations were made.

With the two-element tube, the lines and bands flashed in when the arc struck and disappeared when the arc broke. All of the bands observed belong to Group I. of Fulcher's[2] classification as far as his classification extends and were of those for which Dufour found no Zeeman effect. The observations were made for potentials up to 40 volts which probably accounts for the fact that none of the bands of Group II. were observed, except that one member of each of the two pairs of bands which were placed in both groups was observed. The bands of Group II. are those which increase in intensity with the voltage and include those which Dufour found to show the Zeeman effect.

In the tungsten furnace, the lines flashed in when the arc struck, as low as 10.6 volts, and were strongly reversed in the intense arc of the furnace. The bands did not appear when the furnace was hot and the gas was practically completely dissociated. This is additional evidence that the line spectrum is due to the atom and the band spectrum to the molecule and is in agreement with the conclusions of G. P. Thomson[3] as a result of an investigation of the spectrum emitted by positive rays in hydrogen.

Fulcher's work shows that there are at least two groups of bands in the second spectrum of hydrogen, and Merton[4] suggests that there are three. There are several possible explanations for the different kinds of bands; all of them attributing the radiation to the molecule, as follows: One, or both, of the electrons of a neutral molecule may be set radiating as a result of their disturbance by an electron impact which does not dissociate or ionize the molecule, or by the recombination of an electron with an ionized molecule, or by the recombination of two neutral atoms. It is by the recombination of neutral atoms that Strutt suggests the glow

[1] Langmuir, Irving, Amer. Chem. Soc. Jour., 34, p. 860, 1912, and 37, p. 417, 1915.

[2] Astrophysical Journal, 37, p. 65, 1913.

[3] Phil. Mag., 40, p. 240, 1920.

[4] Royal Society Proc., A, 96, 382, 1919.

of active nitrogen is produced. The remaining electron of an ionized molecule may be set radiating as a result of its disturbance by an electron impact which does not produce dissociation, or by the union of a neutral atom and an ionized atom. There was no means of testing any of these proposed explanations from the data of the investigations reported. I merely wish to point out that there are possible mechanisms for the radiation of several kinds of bands by the hydrogen molecule. The H_3 molecule, which is often present in positive rays in hydrogen, offers additional possibilities for band spectra, and Wendt and Landauer[2] suggest that it may be the source of the bands observed by them.

ARCS IN NITROGEN.

Nitrogen was generated by the reaction of sodium nitrite and ammonium chloride. It was passed through a tube of hot copper turnings and collected over distilled water. Before being admitted into the experimental tube it was passed over phosphorous pentoxide and through a tube immersed in liquid air.

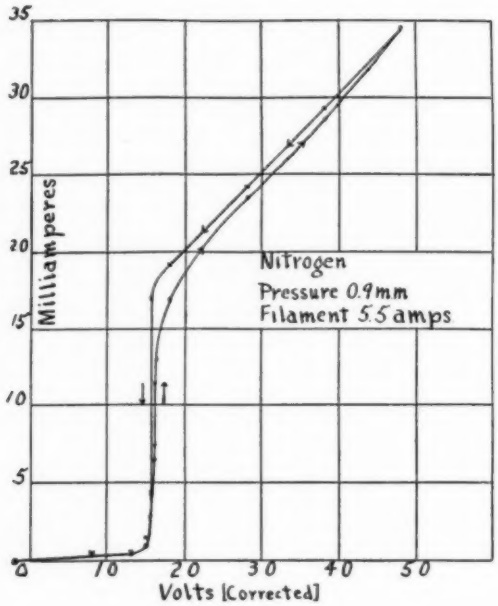


Fig. 11.

The curves obtained for nitrogen, Figs. 11 and 12, are similar in most respects to those for hydrogen when the simple tube was used. The striking potential was higher than the ionizing potential for high gas

[2] Amer. Chem. Soc. Jour., 44, 510, 1922.

pressures, but there was less definite evidence of an apparent saturation current before the arc struck. The difference between the striking and breaking potentials was less in nitrogen than in hydrogen for the same mean free path of electrons. These differences are probably due to the greater elasticity of impact and consequently to the greater space charge

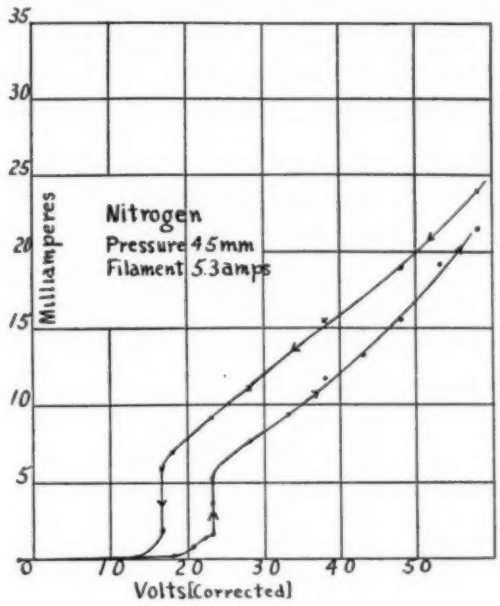


Fig. 12.

in hydrogen than in nitrogen, combined with the greater effectiveness of nitrogen positive ions in neutralizing the space charge of electrons. The current continues to increase quite rapidly with the voltage after

TABLE II.

	Davis & Goucher.[1]	Smyth.[2]	Found.[3]	Mohler & Foote.[4]	Stead & Gosling.[5]	Brandt.[6]	Boucher.[7]
Resonance Potentials.....	7.5 9.0	6.29 7.3 8.29		8.18		7, 8.5	8.4
Ionization Potentials.....	18	18	15.8	16.9	17.2	17.75	15.8

[1] PHYS. REV., 13, 1 (1919).
[2] PHYS. REV., 14, p. 409 (1919).
[3] PHYS. REV., 16, p. 41 (1920).
[4] Jour. Optical Soc. of Amer., 4, p. 49 (1920).
[5] Phil. Mag., 40, p. 413 (1920).
[6] Zeit. für Phys., 8, p. 32 (1921).
[7] PHYS. REV., 19, p. 189 (1922).

the arc has set in, while in hydrogen the current did not increase much after the arc had struck. It was impossible to maintain the arc at potentials lower than the ionizing potential, and the average of the break points was 16.15 volts, which is within the range of ionization potentials reported for nitrogen as shown in Table II.

It was impossible to maintain the arc at lower potentials in the tungsten furnace and so it was concluded that the degree of dissociation of nitrogen at the temperature of the furnace was small. This is in agreement with the conclusion reached by Langmuir[1] for the heat of dissociation of nitrogen.

When the filament was quite hot, the conductivity of the arc increased very rapidly for voltages of 70 volts or more, and, with no further change in the control rheostats, the current increased enormously while the voltage decreased and the arc turned into a brilliant "flare." When the rheostat was operated so as to normally increase the potential across the arc, the voltage decreased instead and the current increased. In this manner a current of more than 15 amperes was obtained at a voltage of about 25 volts. There was a rapid wasting of the tungsten filament in the flare and the nickel anode and the leads supporting the filament were usually quickly melted. By using a tungsten anode and five tungsten filaments in parallel, the flare was maintained for a considerable time and its spectrum studied. Besides the spectrum of nitrogen, the spectrum of tungsten showed up strongly. A black deposit accumulated on the walls of the tube which appeared to be tungsten nitride. The wasting of the filament was not sufficiently rapid to justify the conclusion that the arc was now maintained in tungsten vapor, and so a more probable explanation was sought.

As the conditions in the arc are similar to those in a condensed discharge in a vacuum tube, it was concluded that "active" nitrogen was formed. The excitation of the tungsten spectrum was, then, analogous to the excitation of the spectra of hot metals in "active" nitrogen as accomplished by Strutt,[2] and it was explained by him to be due to the burning of the metals in this nitrogen. He found that this glowing nitrogen has a high electric conductivity, comparable to that of salts in a Bunsen flame, and so this accounts for the increased conductivity of the arc in the "flare." This explanation of the production of the "flare" probably also accounts for the anomalous thermionic emission of tungsten filaments in nitrogen for potentials above 75 volts as discovered by Langmuir.[3]

[1] Amer. Chem. Soc. Jour., 34, 860 (1919).

[2] Royal Soc. Proc., A, 85, p. 219 (1911) et seq.

[3] PHYS. REV., 2, p. 450 (1913).

Strutt concluded that "active" nitrogen is simply monatomic nitrogen and results from the dissociation of nitrogen in the electric discharge. It was possible to get the "flare" in a hot tungsten furnace at a somewhat lower voltage than in the simple tube, *i.e.*, as low as 40 volts instead of 70, and this may be accounted for on this assumption, by a slight increase in dissociation due to the temperature of the furnace. This is the only evidence obtained that there was any dissociation of nitrogen by thermal action.

Spectroscopic Observations on Nitrogen.

Nitrogen has a rich line spectrum and a very complicated band spectrum. The band spectrum has been classified by Deslandres[1] into three positive band spectra and a negative band spectrum. The first positive bands came in with the arc and increased slightly in intensity with the voltage. They have been excited in various ways by slow cathode and canal rays. The second positive bands came in with the arc and decreased in intensity with increased voltage as has also been observed by Fulcher.[2] These bands disappear as the potential is increased, but reappear in the "flare" along with the spectrum of tungsten.

This reappearance can be accounted for on the basis of the explanation of the "flare" as given above, for these bands were found by Fowler and Strutt[3] to be invariably present in the spectrum of the nitrogen afterglow. Besides the second positive bands they find also the first positive bands, with certain groups greatly enhanced, and the third positive bands in the afterglow. They concluded that "active" nitrogen was simply monatomic nitrogen and that the glow was produced by the reunion of the atoms. This manner of excitation corresponds in energy to electron impacts at quite low potentials, very probably less than the ionizing potential.

L. and E. Bloch[4] photographed one of the ultraviolet bands of the second group at 12 volts, which is considerably under the ionizing potential of nitrogen. Erich Brandt[5] by using a four-element tube and varying the potential by intervals of 0.05 volt got a series of discontinuities in the galvanometer current for voltages between 7.5 and 8.2 volts. By applying the $h\nu$ relation to these discontinuities he constructed a band which agrees in frequency difference with some of the positive bands. He found this band characteristic of these discontinuities to persist beyond the ionizing potential and concluded that the

[1] Comptes Rendus, 101, p. 1256, 1885 et seq.
[2] Astrophys. Jour., 37, p. 60 (1913).
[3] Roy. Soc. Proc., A, 85, p. 377 (1911).
[4] Comptes Rendus, 170, p. 1380 (1920).
[5] Zeit. für Phys., 8, p. 32 (1921).

nitrogen molecule is ionized without dissociation. A survey of the various ways in which the positive bands are excited indicates that they can all be excited at less than the ionizing potential and so must be due to the neutral molecule.

The negative bands appear a volt or two above the ionizing potential and increase markedly in intensity with the voltage. Three bands not previously reported were observed at 5075, 5018 and 4961 Å. in good agreement with their calculated positions. The negative bands appear intensely only in regions of strong ionization and positive space charge and must, therefore, be due to the ionized molecule.

At about 70 volts the green doublet 5006, 5003 of the line spectrum appeared faintly and increased in intensity with the voltage. At 90 volts it was quite strong and the yellow lines 5680 and 5667 were also seen. None of the other strong lines were observed although the regions in which they lie were thoroughly searched.

It is difficult to account for the non-appearance of the line spectrum even in the "flare" at potentials less than 70 volts. It may be impossible to dissociate the molecule and ionize one of the atoms at a single impact. Sir J. J. Thomson,[1] from a consideration of the Doppler shifts of the lines in positive rays in nitrogen, concluded that some of the lines, the line 5003 being one of them, are due to the double ionization of the atom and are therefore enhanced lines. This accounts for the high potential required for the excitation of some of the lines but does not explain why so few lines appeared. Perhaps a grouping of the lines in series will clear the matter up. A more complete discussion of the excitation of the spectrum of nitrogen will be published in the Astrophysical Journal.

ARCS IN IODINE.

Chemically pure iodine was resublimed into a bulb having a thin wall. The distilling apparatus was kept connected to a diffusion pump through two liquid air traps, and the sublimation was carried on at a very low pressure. After a sufficient amount had been condensed, the tube was sealed off under a vacuum and then sealed into a second bulb which was connected to the experimental tube. After all the parts had been heated to clean up the surfaces, the iodine was liberated by breaking the thin-walled bulb by means of an iron weight lifted by a magnet.

The vapor pressure of the iodine in the experimental tube was controlled by means of a water bath. When the simple tube was employed, the tube containing the iodine was kept at the temperature at which iodine has the vapor pressure desired. The pressure was determined

[1] Rays of Positive Electricity.

from the curve of Baxter and Gose.[1] In the case of the furnace tube, a considerable amount of iodine was driven into the experimental tube, and allowed to condense on metal end pieces which were water-cooled. The iodine vapor passing out of the tube during a run acted as a diffusion pump and carried off gaseous impurities from the tube. These end pieces were of large area and were kept at the temperature desired, while the bulb containing the iodine originally was maintained at a higher temperature. In both cases the experimental tube was kept connected to a diffusion pump through two liquid air traps. A short piece of capillary tubing was inserted between the experimental tube and the first trap to prevent too rapid loss of iodine, and to insure the desired pressure. When two liquid air traps were used, no difficulty was experienced in keeping mercury out of the apparatus; whereas when only one trap was employed, mercuric iodide invariably appeared after a time.

With the simple tube, the arc struck at or above an average of 14.6 volts and broke at this potential. The pressure was varied from 0.5 to 1.5 mm., the deviation of the critical potential from the average given above being 0.3 volt in the four runs made. With the tungsten furnace, the arc struck at from 10.25 to 36.5 volts depending upon the condition of the tube. As this tube could not be baked out on account of its construction, it was impossible to get entirely free from impurities, although the furnace was run for a considerable time and the tube heated from the inside in this way for two hours before iodine was admitted. The presence of a slight amount of impurity seemed to be sufficient to prevent the striking of the arc at 10.25 volts. On two occasions, once with vapor pressure of 0.3 mm. and the other time at a pressure of 1 mm., the arc was maintained to 10.25 volts. In the former of these runs the arc also struck at this potential. In both cases the filament was as hot as it could be used with safety. In a number of runs the arc struck at about 12 volts, and the average of the breaking potential of 16 runs was 12.1 volts, indicating that this is undoubtedly a critical potential for iodine. Several of the runs showed three sharp discontinuities in the current-potential curve, but there was no agreement in the values of the higher potentials. Iodine probably has several critical potentials, and further investigation to determine them is desirable. It is not surprising that this is the case with so complex an atom as the iodine atom is known to be.

There is no doubt that the iodine was dissociated in the tungsten furnace. Ordinarily the furnace was maintained at a bright yellow heat. Higher temperatures were tried, but there were no differences in the

[1] Amer. Chem. Soc. Jour., 37, 1016, 1915.

critical points obtained. In fact, the heat of the filament and the action of the arc were sufficient to produce practically complete dissociation inside the furnace cylinder. Calculations based upon the work of Starck and Bodenstein[1] on the thermal dissociation of iodine indicate that the vapor would be completely dissociated at pressures up to 5 mm. at 1200° C.

Why it was so difficult to maintain the arc below 12 volts is not clear in as much as the ionizing potential of the iodine atom is usually put at 10 volts or less as is seen from Table III. Compton and Smyth made no attempt to distinguish between radiation and ionization, and, as the total

TABLE III.

	Radiating Potential.	Ionizing Potential.
Found[2]	——	8.5
Mohler and Foote[3]	2.34	10.1
Compton and Smyth[4]	——	8.0 atom 9.4 molecule 6.8 fluorescing molecule

effect in their experiments was small, the ionization produced at the lower potentials may have been due to cumulative action. They point out in their paper that an inspection of Found's published curves shows that there are two break points, a pronounced one at 9.8 volts and another less sharply defined at about 8.3 volts. It would seem, then, that ionization is first definitely detected at about 10 volts, and the 10.25-volt break obtained in this investigation agrees with this within the limits of experimental error. There is no evidence in a comparison of the results of the simple tube and the furnace tube that the molecule is dissociated and one of the atoms ionized at a single impact as there was in the case of hydrogen. While the critical potential obtained from the simple tube is higher than those of the furnace tube, the differences do not correspond to the heat of dissociation of iodine which is equivalent to approximately 1.5 volts. This was a rather surprising result in view of the evidence obtained on this point by Compton and Smyth.

Iodine vapor acts quite rapidly on hot tungsten, and the life of a filament or a furnace was short. This made frequent renewals necessary, and so the progress of the investigation was slow and difficult.

[1] Zeit. Elektrochemie, 16, 966, 1910.
[2] PHYS. REV., 16, 41, 1920.
[3] PHYS. REV., 15, 321, 1920.
[4] PHYS. REV., 16, 501, 1920.

SPECTROSCOPIC OBSERVATIONS ON IODINE.

The line spectrum only appeared in the iodine arc, no trace of any bands being found. With the simple tube a few faint lines appeared, but most of the strong lines were seen with the furnace tube. A few lines flashed in when the arc struck and remained quite strong until the arc broke. The line 4862 was the strongest and most persistent of these and this together with the others of this group have been identified with the "arc" lines listed by Wood.[1] A number of additional lines appeared at higher voltages and increased more rapidly in intensity than those which appeared first. These lines faded out gradually as the voltage was diminished and vanished before the arc broke. They have been identified with other strong lines listed by Wood, being of those which increased in intensity when a spark gap was connected in parallel with his vacuum tube. This manner of appearance suggests that the first lines to appear are due to the neutral atom while the lines coming in later are due to the ionized atom and are enhanced lines. On the basis of the structure of the iodine atom given by the Lewis-Langmuir theory one would expect successive ionizations to occur rather easily.

In conclusion, the writer wishes to express his appreciation to Professor K. T. Compton, under whose direction this work was done, for his many helpful suggestions and unfailing interest during the course of this investigation.

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[1] Researches in Physical Optics, Part II.

AN EXPERIMENTAL STUDY OF THE SCATTERING OF APPROXIMATELY HOMOGENEOUS X-RAYS BY POWDERED CRYSTALLINE CARBON, METALLIC LITHIUM, AND LIQUID BENZENE, MESITYLENE, AND OCTANE.

BY C. W. HEWLETT.

SYNOPSIS.

Scattering and Absorption of Homogeneous X-Rays by Carbon (Diamond and Graphite), Metallic Lithium, and the Liquids Benzene, Mesitylene and Octane.—1. *Scattering curves.* The intensity of the radiation scattered by the substance contained in a small capsule placed at the center of the spectrometer was measured by the ionization method for angles from 2° to 165°. While a ZrO_2 screen was used to isolate the K_α line of Mo (0.712 Å.), some radiation of λ 0.445 Å. was apparently also present. For diamond, graphite and lithium, the maxima agree in position and relative intensity with those found by A. W. Hull by the photographic method. The curves for the liquids, however, are remarkable in that each shows one maximum; 8.5° for benzene, 6.5° for mesitylene and 8.1° for octane, with indications of others unresolved, suggesting that the liquids have a crystal structure. For very small angles the scattering is zero for the solids, and approaches zero for the liquids. 2. *Mass-scattering coefficients* were obtained by integrating the area under the curves, or by experimentally integrating the ionization for all angles of scattering. The coefficients for carbon (diamond and graphite), 0.200, and for lithium, 0.168, agree with Thomson's theoretical values. For benzene, mesitylene, and octane, however, the values 0.238, 0.244, and 0.262 respectively are about ten per cent. larger than those predicted by theory, and give too large specific values for carbon and hydrogen, 0.22 and 0.46 instead of 0.20 and 0.40 respectively. The results are probably accurate to three per cent. 3. *True mass-absorption coefficients*, obtained from the total absorption, the scattering and the density, are found for the solids to be in accord with the theoretical expression $KN^3\lambda^3$, the mean value of K being 4.38×10^{-3}.

Evidence of crystal structure of liquids seems to have been found in the scattering curves for benzene, mesitylene and octane, as suggested above, and the spacings of the planes of atoms responsible for the principal maximum are benzene 4.8 Å., mesitylene 6.3 Å., and octane 5.0 Å.

INTRODUCTION.

THE experiments described in the following report are the outgrowth of a former series of experiments made by the writer[1] in which the mass absorption and mass-scattering coefficients of homogeneous x-rays were studied for several substances as a function of the wavelength of the x-rays. The definitions of these coefficients, and a discussion of the expression $KN^3\lambda^3 + (\sigma/\rho)$ which has been proposed to give the value of the total mass absorption coefficient of x-rays of wave-

[1] PHYS. REV., N. S., 17, 1921, p. 284.

length λ in an element whose atomic number is N, is given in the paper referred to above. In this former work the total mass-absorption coefficient was measured by determining the intensity of a beam of homogeneous x-rays before and after passing through a screen of the absorbing element. The mass-scattering coefficient deduced from the above equation was found to depart from the theoretical value deduced by J. J. Thomson,[1] and the value of K to depend on the scattering element. Moreover the curves were not found to be linear with λ^3 as they should have been in the region investigated according to theoretical considerations. In particular there seemed to be something anomalous in the behavior of carbon in the neighborhood of wave-length 0.75 Å. which is near the K_α line of molybdenum 0.712 Å. The scattering of hydrogen calculated from the experiments on water and liquid oxygen, and the absorption coefficient of lithium could not be interpreted in the light of theory. It therefore seemed advisable to measure the mass scattering, and the true mass-absorption coefficients for certain elements and wave-lengths independently of one another. The present work, of which a preliminary report[2] was made last November before the American Physical Society, consists of measurements of the scattered x-rays as a function of the angle of scattering from graphite, diamond, lithium, and three liquid compounds of carbon and hydrogen. The radiation falling on the scattering material was the x-radiation from a molybdenum anode tube excited at about 30 kv. The radiation was filtered through a screen of zirconium oxide which absorbed very greatly all the radiation except that in the neighborhood of the K_α line of molybdenum.

The general results of the measurements have been expressed in two ways. The intensity of scattering has been plotted as a function of the angle of scattering, and the mass-scattering coefficients and the true mass-absorption coefficients have been tabulated together with other data from which they were directly deduced.

The matter is presented in the following order:

I. Description of Apparatus and Mounting of the Scattering Material.
II. Procedure in the Experiments.
III. Procedure in Calculating the Mass Scattering and the True Mass-Absorption Coefficients.
IV. Sources of Error.
V. Results and Discussion.
VI. Appendix; a Detailed Consideration of a Point arising in III.

[1] Conduction of Electricity through Gases, 2nd edition, p. 325.

[2] Phys. Rev., N. S., 19, 1922, p. 265.

Description of Apparatus and Mounting of Scattering Material.—The Coolidge tube was mounted on sulphur insulators in a lead-covered wooden box about 2 ft. x 2 ft. x 3 ft. The tube was supplied by a 35 kv. oil-insulated transformer which in turn was supplied by a motor generator set. Regulation of voltage and frequency were obtained by rheostats inserted in the field circuits of the motor generator. A D'Arsonval type milliammeter was inserted in the secondary of the transformer at its midpoint which was grounded. All of the high potential apparatus was enclosed in a wire netting cage and the door into this cage could not be opened without opening the primary circuit of the transformer.

The x-ray spectrometer was constructed in this laboratory, and angular settings could be made with an accuracy within 2′ of arc. The ionization chamber was mounted on wheels so that it could rotate about the axis of the spectrometer. The scattering material was mounted in a small celluloid capsule whose axis coincided with that of the spectrometer. The small table holding the scattering material was caused to rotate continuously about the axis of the spectrometer.

The ionization chamber was 1 foot long. The outside brass cylinder was 4 inches in diameter and was earthed. The inside cylinder was $3\frac{3}{4}$ inches in diameter, and was kept charged to a potential of about 250 volts by a battery of dry cells. A horizontal electrode insulated by amber was placed in this inner cylinder about half way between its axis and surface. A fine wire was soldered to this electrode and then passed along the axis of a brass tube leading from the ionization chamber to a point in the axis of the spectrometer about 6 inches above the scattering material. From this point the wire passed down the axis of another tube to one pair of quadrants of an electrometer. The movable and fixed tubes were connected by end pieces, one of which could rotate inside the other. The wire joining the electrode to the electrometer was insulated by amber throughout and was completely shielded, all of the shielding being connected together by soldered wires and grounded. The opening in the ionization chamber was 1.50 cm. in diameter, was situated in the horizontal plane passing through the x-ray beam and scattering material and the distance of this opening from the scattering material was 35.5 cm. The electrodes in the ionization chamber were so placed that none of the x-rays from the scattering material could strike them. A lead screen was placed about half way between the scattering material and the opening in the ionization chamber. An opening in this screen was made just large enough to allow every part of the scattering material to send x-rays to every part of the opening. A lead hood was placed over the space between the ionization chamber and this screen to cut off

possible radiation from other objects than those in the neighborhood of the axis of the ionization chamber. In order to cut off all unnecessary direct x-radiation there were two lead slits between the box and the scattering material, the one nearest the scattering material being about 10 cm. distant.

The other pair of quadrants of the electrometer were connected to the case of the electrometer and to earth. An earthing key was connected through a resistance of about 1,000 ohms to earth. This resistance was connected to a potentiometer so that the key could be charged to any desired potential or earthed at will. This key dipped into a mercury cup connected to the electrode in the ionization chamber. The electrometer needle was charged to a potential of 100 volts, and the sensitivity ranged from 1,000 to 5,000 divisions per volt in the different parts of the work.

The scattering material was mounted in thin cylinders of circular cross section, which were made by cutting sheet celluloid of 1 mil thickness into strips from $\frac{1}{8}$ to $\frac{3}{8}$ inch in width and wrapping them helically on a brass or steel rod, allowing each turn a narrow lap on the preceding one. This helix was then secured at each end and the helical seam cemented with collodion. These capsules were found to absorb less than one per cent. of the x-rays falling on them. Two sizes of capsules with internal diameters of $\frac{3}{16}$ and $\frac{1}{4}$ inch were used.

The material called artificial graphite was a highly purified carbon which was obtained in compressed cakes. It was finely powdered by filing, and the powder packed into the capsule. The natural graphite was originally in chunks. This material was forced through a sieve of 50 meshes to the inch, and then packed into a capsule. The diamond was in the form of five splints. These splints were very thin and their cross-sectional area ranged from 0.010 to 0.001 sq. cm. The lithium, from a very old exhibition sample, of German manufacture, was squirted through a die into a rod of the required dimensions, and immediately enclosed in one of the celluloid capsules. Fortunately none of the three liquids used in these experiments attacked the capsules.

II. Procedure in the Experiments.

Method of obtaining the data for plotting the curves. The beam of x-rays, which had a rectangular cross section, was adjusted so as to cover the whole width of the capsule of scattering material and to project a short distance on either side. The cross section of the beam in the vicinity of the scattering material was approximately 0.8 cm. square, but this was varied slightly from time to time when different size capsules were used.

The x-ray tube was operated at a potential of about 30 kv. at 60.7 cycles per sec. and the current read on a D'Arsonval type milliammeter was 4 m.a. These conditions of operation were maintained constant to within 1 per cent. throughout the work. A zirconium oxide screen, which reduced the K_α line to about 60 per cent. of its intensity without the screen, and reduced the K_β line to about 6 per cent. of the intensity of K_α line, was placed in the path of the radiation as it emerged from the box containing the tube.

The ionization chamber was set at as small an angle as could be done without allowing any of the direct beam to enter it, the electrometer was charged, the earth connection broken, and the time required for the electrometer deflection to change from one of two definite values to the other was determined. An empty capsule of the same construction as the one containing the scattering material was then substituted for the full capsule, and the time required for the same change in deflection determined. Deducing the rates of deflection, and subtracting that due to the empty from that due to the full capsule, the rate of deflection due to the scattering material was obtained, and this was taken as a measure of the intensity of the scattered radiation entering the ionization chamber. If the intensity was so great that the rate of deflection was no longer an accurate measure of its intensity, the following method was adopted. A lead screen was placed between the scattering material and the ionization chamber, the electrometer charged, the earth connection broken, and the deflection noted. The lead screen was then removed for a definite interval of time and then replaced. When the deflection became constant its value was again noted. Whenever necessary, account was taken of the rate of deflection with the lead screen in place. In this way the intensity was determined from point to point, the steps in most cases being less than the angle subtended by the opening in the ionization chamber at the scattering material, particularly in the region of a pronounced maximum. When once the position of the principal maximum of scattering was known, measurements were made frequently at this setting, to check the constancy of operation. Finally the intensity at the various angles was expressed as percentages of the intensity at the principal maximum.

In order to calculate from the scattering curve the fraction of the incident energy which was scattered it was necessary to know the ratio between the flux of radiation into the ionization chamber at some particular setting and the flux of energy falling on the scattering material; and in addition, the total mass-absorption coefficient of the radiation in the scattering material. These quantities were usually determined at

the beginning and at the end of each series of measurements of the intensity. Two methods were used in determining the above ratio and the total mass absorption coefficient.

In the first method a thin lead sheet through which had been bored a circular hole about 0.10 cm. in diameter was placed immediately behind the capsule so that the beam of x-rays through the hole passed through the axis of the capsule. A lead disc mounted on the axle of a small electric motor was placed between the capsule and the ionization chamber with its face perpendicular to the beam of x-rays. The axis of the ionization chamber was set to coincide with that of the beam of x-rays. There was a narrow radial slit in the disc so that when the disc was in rotation the small beam passing through the circular hole entered the ionization chamber for a short interval once during each revolution of the disc. By this means it was found possible to secure a conveniently measurable fraction of the energy flux falling on the capsule. This fraction of the energy flux was calculated from the cross section of the x-ray beam striking the capsule when unobstructed by the lead sheet, the area of the hole, and the angular width of the slit in the lead disc. The cross section of the x-ray beam falling on the capsule was deduced from an x-ray shadow picture made by the x-ray beam on a photographic film placed perpendicular to the x-ray beam and in contact with the full capsule, the beam passing first through the capsule, then striking the film. The width of the shadow of the capsule checked with the diameter of the capsule. The diameter of the hole was measured with a micrometer microscope. The total mass-absorption coefficient of the radiation in the scattering material was determined from measurements of the energy flux through the small hole and rotating disc, determined alternately when the x-rays passed through the full and the empty capsule.

There are two objections to the method outlined above; namely, a flash of x-rays entering the ionization chamber is not representative of the average intensity of the beam, but is a very small section of the radiation emitted during one cycle of the alternating current. The number of these flashes received by the chamber during a determination is very large, however, and unless the disc should have a speed bearing a simple relation to the frequency of the alternating current from the transformer, this consideration should not lead to undesirable results. On the other hand, the thin lead screen with the small hole had to be adjusted very accurately perpendicular to the x-ray beam, for it had a thickness comparable with the diameter of the hole. This consideration led to the adoption of another method for determining the total mass-absorption coefficient and the ratio of the energy flux falling on the capsule to that entering the ionization chamber at a definite setting.

The following method was designed to allow the total energy flux falling on the capsule to pass into the ionization chamber for the time of one complete cycle of the alternating current from the transformer. A lead disc carrying an angular slit of adjustable width was mounted on a horizontal axle, so that in rotating, the beam of x-rays was allowed to pass through the slit when the latter was vertical. This disc and axle was controlled by a stiff steel helical spring in the same manner as the balance wheel of a watch. Two stops with trigger action were arranged so that one of them could hold the disc displaced from its vertical position by a definite amount, and upon release, the other stop would catch and hold the disc at the end of its first swing. By successive adjustments of the stiffness of the spring, the width of the slit, and the height of the stops, the time for the slit to sweep across a point in the x-ray beam was made equal to the period of the alternating current to within 1 per cent. In order to determine when the adjustment was completed, the face of the disc was covered with a thin film of smoke and a vibrating reed operated by the alternating current supplying the transformer traced a curve on the disc as it swung. The disc was mounted close to the box containing the tube, where the cross section of the beam was a minimum. Obviously it makes no difference what part of the cycle the exposure begins if it lasts one complete cycle.

A lead slit open at the lower end and having a width equal to that of the capsule was placed on the capsule when making measurements of the direct beam, so that only the portion of the beam striking the capsule could pass on to the ionization chamber. The opening in the ionization chamber was large enough to receive all of the radiation which passed through the capsule, and the exact position of the chamber was secured with the aid of a fluorescent screen.

The procedure was as follows: with the empty capsule in place the lead disc was secured by one of the stops. The electrometer was charged, the earth connection broken, and the electrometer deflection noted. The stop was tripped, allowing the disc to swing. The deflection of the electrometer changed rapidly, and became constant again in about one minute, at which time its value was again noted. From the change in deflection the charge given to the insulated system was computed, and this was taken as a measure of the radiation falling on the capsule during one cycle. The full capsule was then substituted for the empty one, and the procedure repeated, from which was computed the radiation transmitted through the scattering material during one cycle. A number of such determinations were made at each experiment, those with the empty and full capsules being distributed in such a manner that the mean

values of each corresponded to the same epoch. The intensity of the scattered radiation for the principal maximum of the scattering material was next determined in the manner already described.

By multiplying the ordinates of a scattering curve by the sine of the angle of scattering, and by a factor to take account of the size of the angular opening of the ionization chamber measured from the scattering material, a new curve was obtained, the area under which gave the total amount of scattered radiation in terms of the radiation falling on the scattering material. This procedure rests upon the assumption that an element of the scattering material containing a large number of small crystals would scatter radiation equally in all directions making a given angle with the direction of the direct beam.

The following method was devised so that the procedure of calculation from the scattering curve just described would be done automatically by the method of measuring the scattering. Having first measured the intensity of the direct beam through the empty and full capsules, the ionization chamber was set close to the direct beam. With a lead screen in front of the chamber the electrometer was charged, the earth connection broken, and the deflection noted. At a definite instant, which was recorded beforehand, the lead screen was removed and the ionization chamber moved along from degree to degree, leaving it on each degree for an interval of time proportional to $\sin \theta$, where θ was the angular setting of the chamber from the direct beam. The schedule for moving the chamber was prepared beforehand, and was so designed that the amount of radiation entering the ionization chamber during its tour around the circle was equal to the total amount of radiation scattered in 1 second.

The total charge taken by the electrometer during its tour around the circle was then proportional to the total x-rays scattered during 1 second. This total charge was deduced from the total change in deflection of the electrometer. This procedure was carried through for the empty capsule and for the full capsule in such a manner that the results for each corresponded to the same epoch. At the end, the intensity of the direct beam was again measured through the empty and full capsules.

III. Procedure in Calculating the Mass-Scattering Coefficient and the True Mass-Absorption Coefficient.

1. Calculation of the total mass-absorption coefficient $(\mu + \sigma)/\rho$. The densities of the materials in the capsules were determined, in the case of the solids, by dividing the mass of the material packed in the capsule by the volume of the capsule; in the case of the liquids by finding the loss in weight of a sinker of known volume when suspended in them.

When the small hole and rotating disc were used for measuring the total mass-absorption coefficient, this quantity was given by the expression

$$d = \epsilon^{-\frac{\mu+\sigma}{\rho} \cdot t},$$

where t is the average length of path of the x-rays through the scattering material, and d is the ratio of the intensity of the beam through the full capsule to that through the empty capsule.

When one cycle of the x-rays falling on the capsule was allowed to enter the ionization chamber the total mass-absorption coefficient was calculated from the following expression:

$$d = 1 - \frac{\pi}{4} b + \frac{1}{3} b^2 - \frac{\pi}{32} b^3 + \frac{1}{45} b^4 - \cdots,$$

where

$$b = \frac{\mu + \sigma}{\rho} D.$$

D is the diameter of the capsule.

2. Calculation of the fraction of the x-rays falling on the scattering material that was scattered. When using the scattering curves the first procedure was to multiply the ordinates of the scattering curve by the factor

$$\frac{2 \sin \delta}{1 - \cos \delta} \sin \theta,$$

where δ is half the plane angle subtended at the scattering material by the opening in the ionization chamber, and θ is the angle from the direct beam at which the scattering was measured. The area under this new curve was then found, using 2δ as the unit abscissa and 100 per cent. as the unit ordinate. This area is equal to the total measured scattered x-rays in terms of that measured at the angle of maximum scattering. The number for the total measured x-rays was then corrected by estimation for the scattering between 165° and 180° inaccessible to the ionization chamber. This correction usually amounted to 1 or 2 per cent. of the total measured x-rays. Next the correction for absorption in the scattering material (see appendix) was applied, giving the total scattered x-rays in terms of that measured at the angle of maximum scattering. Finally, this number was divided by the ratio of the energy flux falling on the scattering material to that entering the ionization chamber at the angle of maximum scattering, giving the fraction of incident x-rays that was scattered.

When the scattering was measured by rotating the ionization chamber

from degree to degree the total measured scattered x-rays for the empty capsule were subtracted from that for the full capsule, and the corrections for the region inaccessible to the ionization chamber and for the absorption in the scattering material were applied. This gave the total x-rays scattered in 1 second which was then divided by the x-rays falling on the scattering material in 1 second.

3. Calculation of the mass-scattering and the true mass-absorption coefficients. When one cycle of the radiation falling on the capsule was allowed to enter the ionization chamber, the amount of the direct beam taken out by the scattering material is given directly by $1 - d$. When the small hole and rotating disc was used the fraction of the direct beam of x-rays taken out by the scattering material was calculated from the expression

$$\frac{\pi}{4}b - \frac{1}{3}b^2 + \frac{\pi}{32}b^3 - \frac{1}{45}b^4 + \cdots,$$

where

$$b = \frac{\mu + \sigma}{\rho} D.$$

Let this fraction be denoted by T, while S denotes the fraction of the incident beam scattered. Then since scattering and absorption take place together

$$\frac{S}{T} = \frac{\sigma}{\mu + \sigma},$$

so that the mass-scattering coefficient is given by

$$\frac{\sigma}{\rho} = \frac{S}{T} \cdot \frac{\mu + \sigma}{\rho}.$$

Each of the three quantities on the right were measured so that σ/ρ could be calculated. The true mass-absorption coefficient was then obtained by subtracting the mass-scattering coefficient from the total mass-absorption coefficient.

IV. Sources of Error.

1. On account of the finite size of the scattering material there is some indefiniteness as to its centroid. The volume of the scattering material was about 0.10 cm.^{3} and 0.20 cm.^{3} for the smaller and larger capsules respectively.

2. The x-rays were not parallel at the scattering material, so that the total mass-absorption coefficients as calculated would be slightly in error. The distance from the source of x-rays to the scattering material was 1 meter.

3. Saturation voltage in the ionization chamber was secured by trial, and then twice that voltage allowed as a factor of safety.

4. The electrometer scale was not absolutely uniform, but the proper corrections were applied wherever necessary.

5. The variation of voltage, frequency, and thermionic current through the tube would introduce serious errors in work of this kind if not carefully controlled. All of these were carefully regulated by hand, frequently one person giving this his entire attention.

6. Variation in the effective amount of methyl bromide in the ionization chamber during a series of experiments. Although this was at times rather large, standardizing measurements were made at the beginning and end of each series, and frequently during the series, so that it was possible to allow by interpolation for uniform changes such as the above.

7. Non-uniformity of the density of the scattering material in the capsules. In the case of the liquids this consideration does not enter, and in the case of the diamond splints it is safe to conclude that the effect is negligible. With the two kinds of graphite every precaution was taken to insure uniformity of distribution by careful packing, and the observations were made allowing the x-rays to fall on different sections of the capsule. In the case of the lithium there is a possibility (hardly probable) of blow holes. These blow holes might even be filled with some of the oil in which the lithium had been kept.

8. The adjustment of the small hole behind the scattering material in the one method for measuring the absorption coefficient and the adjustment of the slit on the scattering material in the other method were made with great care as a small displacement of these limiting devices would lead to a relatively large error in the results.

All of these main sources of error and several other minor ones have been carefully considered and it is estimated that the final results are not in error by more than 3 per cent. on account of them.

V. Results and Discussion.

Table I. gives the results on the mass-scattering and the true mass-absorption coefficients of the substances given in the first column. The second column gives the method used in the determination, the number in brackets showing the number of separate determinations from which the values in a given line were deduced.

Method *A* signifies that the calculations were made from the scattering curve for the material. The comparison with the direct beam of x-rays in these calculations was determined by allowing one cycle of the x-rays

falling on the capsule to enter the ionization chamber. In method *B* the ionization chamber was moved from degree to degree allowing the charge on the electrometer to accumulate. The comparison with the direct beam of x-rays in these calculations was determined by the small hole and rotating disc method. Method *C* differed from method *B* in that the comparison with the direct beam was as in method *A*. The third column gives the percentage *S*, of the x-rays falling on the scattering material, which was scattered. The fourth column gives the fraction *F*, of the x-rays falling on the scattering material, which was removed by the combined processes of absorption and scattering. The fifth, sixth, and seventh columns give the total mass-absorption coefficient, the mass-scattering coefficient, and the true mass-absorption coefficient respectively. The eighth column gives the means of the mass-scattering coefficient for each substance. The ninth column gives the value of *K* calculated from the expression $\mu/\rho = KN^3\lambda^3$ where μ/ρ is the true mass-absorption coefficient.

A comparison of the position of the maxima in the scattering curves for the solid substances shows good agreement with those obtained by Hull [1] using the photographic method. The relative intensities of the

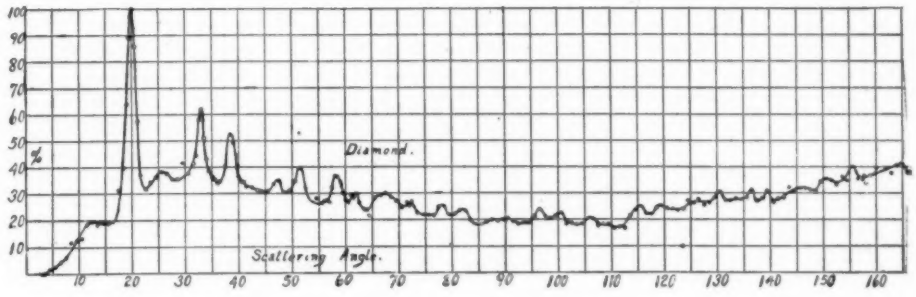

Fig. 1.

various maxima agree as well as might be expected considering the degree of uncertainty that lies in estimating relative intensities from blackening of photographic plates.

A novel point of interest shown by the curves and previously reported by the writer[2] is that for the solid substances the scattering becomes zero for very small angles from the direct beam, and approaches zero for the liquids. A special experiment was carried out to check this fact. A lead slit about 3 mm. wide was placed over the opening in the ionization chamber and it was found that at 2° from the direct beam the liquids

[1] PHYS. REV., N. S., 10, 1917, p. 661.
[2] PHYS. REV., N. S., 17, 1921, p. 284.

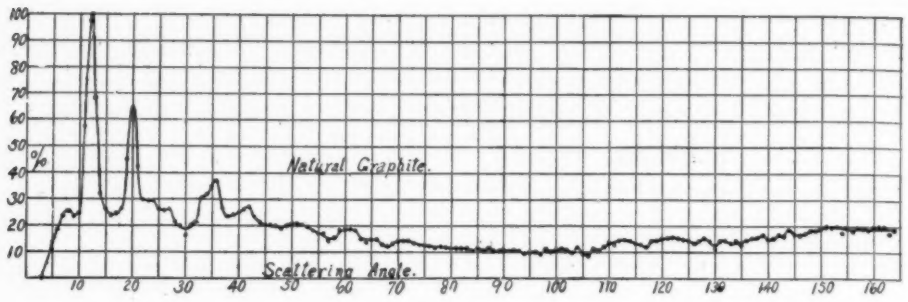

Fig. 2.

scattered less than 10 per cent. as much as at the angle of maximum

TABLE I.

1.	2.	3.	4.	5.	6.	7.	8.	9.
Substance.	Method.	S%.	F%.	$\frac{\mu+\sigma}{\rho}$.	$\frac{\sigma}{\rho}$.	$\frac{\mu}{\rho}$.	Mean $\frac{\sigma}{\rho}$.	K.
Diamond Splints.....	A(1)	11.86	26.1	.428	.195	.233		4.40×10^{-3}
Diamond Splints.....	B(10)	12.16	31.7	.515	.198	.317	.199	4.44
Diamond Splints.....	C(2)	12.19	29.6	.497	.205	.292		4.33
Natural Graphite.....	A(1)	6.55	18.6	.553	.195	.358		4.53
Artificial Graphite....	A(1)	6.33	17.4	.551	.200	.351	.201	4.33
Artificial Graphite....	B(7)	6.49	17.4	.551	.206	.345		4.26
Artificial Graphite....	C(3)	6.35	15.2	.477	.199	.278		4.35
Metallic Lithium.....	A(1)	4.21	5.78	.217	.158	.059	.168	4.36
Metallic Lithium.....	C(4)	4.14	4.80	.206	.178	.028		
Benzene.....	A(1)	9.28	18.6	.478	.238	.240		
Benzene.....	B(3)	6.90	14.7	.497	.233	.264	.238	
Benzene.....	C(3)	6.69	13.8	.468	.227	.240		
Benzene.....	C(1)	9.70	21.6	.567	.255	.312		
Mesitylene.....	A(1)	9.39	18.4	.478	.244	.234		
Mesitylene.....	B(2)	6.83	14.4	.489	.232	.257	.244	
Mesitylene.....	C(2)	7.02	12.8	.431	.236	.195		
Mesitylene.....	C(1)	9.89	21.3	.564	.262	.302		
Octane.....	A(1)	8.05	15.5	.496	.258	.238	.262	
Octane.....	C(1)	8.29	16.3	.524	.266	.258		

scattering, while for graphite and diamond the scattering was zero at angles of 5° and 6° respectively. Since this fact was published, A. H. Compton[1] has given a theoretical discussion in which he has shown that the scattering would be expected to become zero for small angles in the case of crystalline material. A quantitative explanation of this behavior for the liquids is as yet not forthcoming. It will be noticed that there is a prominent maximum which occurs for the solid substances at a smaller

[1] Not yet published.

angle than the principal maximum which corresponds to a wave-length 0.712 Å. Assuming that this maximum at the smaller angle is due to

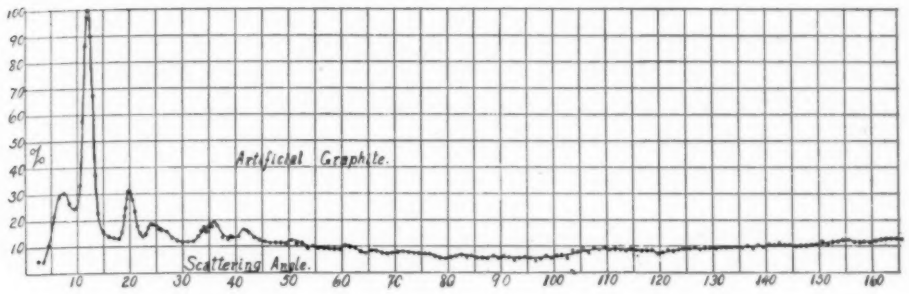

Fig. 3.

the short wave-length radiation which gets through the Zr filter, the effective wave-length was calculated from the data on diamond graphite and lithium supposing that this maximum was due to reflection from the set of planes giving the principal maximum in each case. This gave the effective wave-length of this radiation as 0.446, 0.441, and 0.449 Å.,

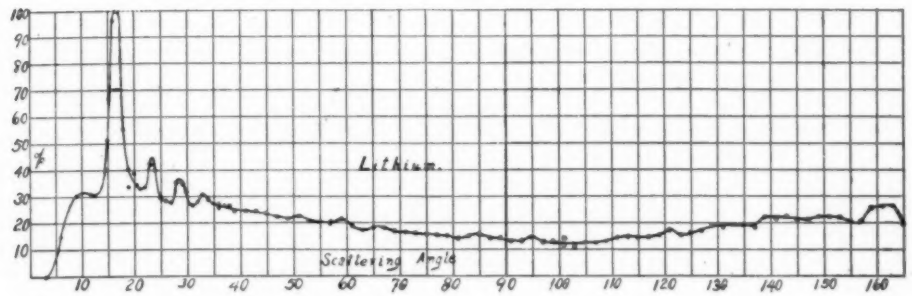

Fig. 4.

for the three substances in the order named. The mean value for this wave-length is then 0.445 Å. This explains the appearance of the maximum occurring in the neighborhood of 25° in the curve for diamond, for this is the correct position for second-order reflection of wave-length 0.445 Å. from the 111 planes.

The appearance of a very pronounced maximum at a small angle for each of the liquids investigated points very strongly toward the view that these liquids have something of a crystal structure. These maxima occur at rather small angles, and consequently the maxima due to the first two or three orders of reflection for the wave-length 0.445 Å. would overlap the first two due to the wave-length 0.712 Å. It will be seen

that this idea readily lends itself to explain the relatively complicated structure of the maxima, and the slightly irregular course of the scattering

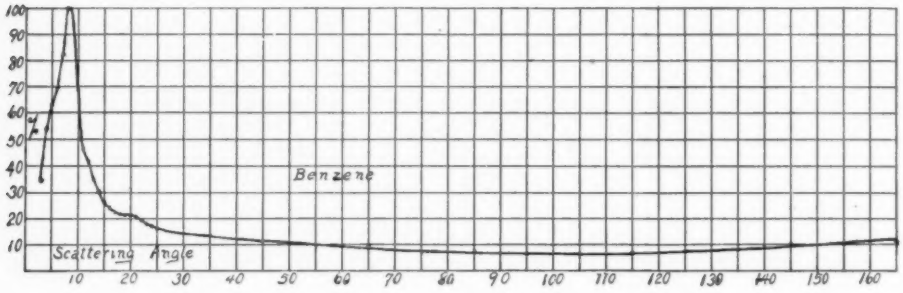

Fig. 5.

curves for the liquids between 10° and 25° scattering angle. The capsules containing the liquids from which these curves were obtained were 0.25 inch in diameter, so that the overlapping would be greater than with the smaller capsules (0.187 inch in diameter) which were used for graphite and diamond. The scattering curves for these liquids for the first 25° have been studied very carefully, using capsules 0.187 inch in diameter, and a slit 3 mm. wide across the opening in the ionization chamber. With this arrangement the complicated structure of the maxima shown in the curves in this paper have been resolved into separate maxima, and the position of the principal maximum due to

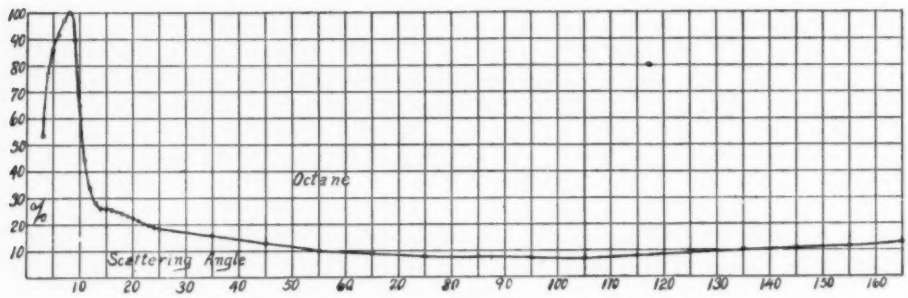

Fig. 6.

wave-length 0.712 Å. found as follows: benzene 8°.5, mesitylene 6°.5, octane 8°.1. The distances between the planes of atoms responsible for these maxima are as follows: benzene 4.8 Å., mesitylene 6.3 Å., octane 5.0 Å.

Very little information can be drawn from the curves in regard to the intensity of reflection from the crystal planes in the successive orders, for the number of sets of planes coöperating at a given angle of scattering

in the case of powdered crystals is too great. Since there are an infinite number of sets of planes in any given crystal lattice, the number of coöperating sets at any given angle of scattering would be very great, and would be greater the smaller the individual crystals of the material. This point is illustrated by a comparison of the curves for natural and artificial graphite. The artificial graphite was more finely powdered than the natural graphite, and the maxima for the latter stand out more prominently than for the former. The curves indicate, however, that the reflections in the successive orders decrease at least as rapidly as the inverse square of the order of reflection.

It should be mentioned that the shape of the scattering curves depends to some extent on the dimensions of the scattering material and the opening in the ionization chamber; the changes in the curves becoming more abrupt the smaller these dimensions. The relative heights of the maxima and minima would also be slightly dependent on these considerations. The radiation falling on the scattering material contains, besides the K_a line of molybdenum, an appreciable amount of shorter wave-length radiation, which fact in itself complicates the interpretation of the curves to a certain extent. With different thicknesses of filtering material the scattering curves would be different. The more homogeneous the radiation the more prominent, and the sharper would be the maxima of the curves. But even with constant filter thickness, dimensions of apparatus, and conditions of tube operation, there is still a factor

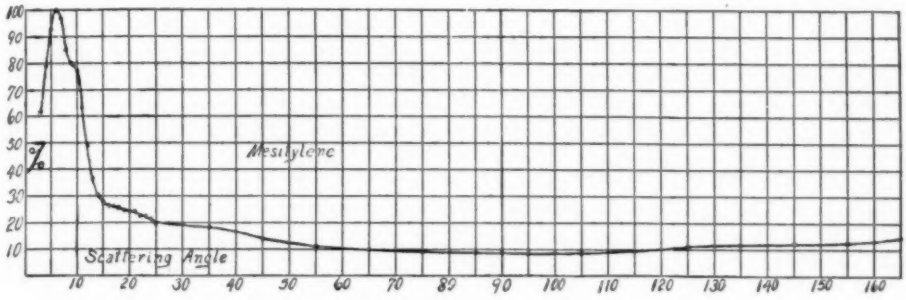

Fig. 7.

which affects the experimental scattering curves. The ionization chamber is not long enough to absorb all the radiation which enters it; especially is this true for the short wave-length radiation. When the ionization chamber had been freshly filled with methyl-bromide gas the short wave-length radiation was absorbed to a much greater extent by the gas than a few days later when the gas had become less susceptible to ionization. The longer wave-length radiation of the K_a line was

absorbed almost to the same extent when the chamber was freshly filled, and for a few days thereafter. It may readily be seen that the experimental scattering curve, with a given distribution of radiation falling on the scattering material, will depend upon the density of methyl-bromide gas in the ionization chamber; the maxima will be sharper and more pronounced, the less the density of the gas. For the sake of uniformity and in order to have large ionization currents which could be measured with accuracy, the curves shown in this paper were determined in the interval between freshly filling the ionization chamber and a time when the ionization current had fallen to half value with a constant intensity of x-rays. In the other part of the work where the ionization chamber was rotated continuously so as to automatically integrate the scattered radiation, the density of the gas in the ionization chamber varied widely. It is noticeable in this connection that although the total and true mass-absorption coefficients varied through a wide range for a given substance the mass-scattering coefficient was nearly constant. This is to be explained by the variation in the amount of methyl-bromide gas in the ionization chamber. Since there is both short and long wave-length radiation present the ionization chamber will give a relatively greater importance to the short wave-length radiation when freshly filled than some time later, so that the effective wave-length for ionization will be shorter the greater the density of methyl bromide in the chamber. According to theoretical considerations the mass-scattering coefficient is independent of the wave-length (over certain regions of wave-length this is not true) while the true mass-absorption coefficient in this region of wave-length should be proportional to the cube of the wave-length.

In order to test the above proportionality, the factor of proportionality was calculated for diamond, graphite, and lithium from the equation $\mu/\rho = KN^3\lambda^3$. The value of λ to be substituted in this equation was determined for diamond and graphite by reading off from the absorption curve for carbon previously published by the writer the wave-length corresponding to the value for the total mass-absorption coefficient. The value of the wave-length for lithium was taken to be the same as that for natural graphite as the conditions of operation were about the same in the two cases. It is noticeable that K is nearly the same for diamond, graphite, and lithium, its mean value being 4.38×10^{-3}. This contradicts the writer's former work on lithium where K and the absorption coefficient were found to be abnormally high. The lithium used in the former experiments must have been impure. At least it is known that potassium chloride was mixed with the lithium chloride in the electrolytic separation of the lithium.

From the data given in the table it is seen that the mass-scattering coefficient for carbon agrees with the theoretical value calculated by J. J. Thomson,[1] the average values for graphite and for diamond agreeing with one another and with the theoretical value, 0.200, within the limit of experimental error. The mass-scattering coefficient is thus seen to be independent of the crystal structure. The mean value for lithium 0.168 comes within 3.5 per cent. of the theoretical value 0.174. The mass-scattering coefficients found for the liquids varied somewhat erratically, moreover they are greater than the theoretical values assuming the mass-scattering coefficient of carbon and hydrogen to be 0.200 and 0.399 respectively. The theoretical values for benzene, mesitylene, and octane are 0.215, 0.220, and 0.231 respectively, while the means of the experimental values are 0.238, 0.244, and 0.248 respectively. Assuming that these experimental mass-scattering coefficients are each made up of two parts, one due to carbon and one due to hydrogen, each part in proportion to the mass of carbon and hydrogen present respectively, the mass-scattering coefficients of carbon and hydrogen were calculated to be 0.228 and 0.375 respectively. The value thus found for hydrogen comes within 6 per cent. of the theoretical value 0.399, while the value for carbon is 14 per cent. higher than the value found for graphite and diamond. The mass-scattering coefficients of the three liquids found by method *A* furnish probably a more just basis for determining the separate coefficients for carbon and hydrogen than the above calculation, for the three curves were determined simultaneously point for point. The three equations for the three substances are:

For benzene	$12C + H = 3.100,$
For mesitylene	$9C + H = 2.440,$
For octane	$16C + 3H = 4.893,$

where C and H represent the mass-scattering coefficients of carbon and hydrogen respectively. These equations give three independent values for C and H.

	C.	H.
	0.220	0.488
	0.221	0.441
	0.220	0.460
Means,	0.220	0.463

It is seen that both the values of C and H are considerably larger than the theoretical values. If these liquids contained very small percentages of some element of moderately large atomic weight, such as bromine,

[1] Conduction of Electricity through Gases, 2nd edition, p. 325.

some of the absorbed x-rays reëmitted as characteristic x-radiation would be of sufficient penetrating power to reach the ionization chamber where it would add to the effect of the scattered radiation. At least this hypothesis is plausible in the case of the octane, for bromine was one of the constituents of one of the compounds from which it was prepared. The origin of the benzene and mesitylene is not known, but their boiling points and densities indicate that they are relatively pure. One might look for some such effect as proposed above by the method devised by A. H. Compton.[2] This was tried at the angle of maximum scattering for benzene with a negative result.

VI. Appendix. Correction for Absorption of the Scattered Radiation within the Scattering Material.

Attempts to arrive at a complete solution of this problem have not succeeded.

Making the usual assumption of exponential absorption of the x-rays, let $(\mu + \sigma)$ be the linear absorption coefficient, where μ represents that part of the coefficient due to true absorption, and σ that due to scattering. Let us suppose that the distance of the source of x-rays from the scattering material is great enough so that the x-rays are parallel in passing through. This condition is sufficiently fulfilled in the present work. It may then be shown that of a beam of x-rays striking a circular cylinder of material perpendicular to its axis, a fraction is scattered per unit solid angle in the direction making an angle θ with the beam, given by the following expression:

$$S_\theta = f(\theta)\left(1 - \frac{4}{3\pi}a + \frac{1}{8}a^2 - \frac{4}{45\pi}a^3 + \frac{1}{192}a^4 - \cdots\right),$$

where $a = (\mu + \sigma)D$ and D is the diameter of the cylinder $f(\theta)$ is a factor depending on the crystal structure, expressing the angular distribution of the scattered radiation. Not all of this scattered radiation gets out of the scattering material because it is absorbed and scattered on its way out. If it assumed that none of S_θ which is rescattered gets out, we arrive at the following expression for the fraction of the original beam getting out of the cylinder per unit solid angle in the direction making an angle θ with the beam

$$S_\theta' = f(\theta)\int_{-R}^{+R}\int_{-\sqrt{R^2+x^2}}^{+\sqrt{R^2-x^2}} \epsilon^{-(\mu+\sigma)[x+\sqrt{R^2-y^2}+\sqrt{R^2-(x\sin\theta+y\cos\theta)^2}-x\cos\theta+y\sin\theta]}\,dxdy,$$

where R is the radius of the cylinder. The origin of coördinates is taken

[2] Phys. Rev., N. S., 18, 1921, p. 96.

on the axis of the cylinder. The above assumption is not justifiable, and consequently S_θ' given above is too small. The first four terms of the expansion in powers of a, of the above integral, which were found for me by Prof. E. W. Chittenden, of the department of mathematics at this university, are as follows:

$$S_\theta' = f(\theta)\left[1 - \frac{8}{3\pi}a + \frac{1}{4}\left(1 - \frac{\cos\theta}{4} + \frac{\gamma(\pi-\gamma)}{2\pi\sin\gamma} + \frac{\pi-2\gamma}{4\pi}\cos\gamma + \frac{\sin\gamma}{\pi}\right)a^2 - \frac{24}{45\pi}\left(1 - \frac{7}{22}\cos\theta + \frac{1}{22}\cos^2\theta - \frac{1}{22}\cos^3\theta + \frac{1}{22}\cos^4\theta\right)a^3\right],$$

$a = (\mu + \sigma)D$

and

$$\gamma = \theta \quad \text{if} \quad 0 \leqq \theta \leqq \frac{\pi}{2},$$

$$\gamma = -\theta \quad \text{if} \quad -\frac{\pi}{2} \leqq \theta \leqq 0,$$

$$\gamma = \pi - \theta \quad \text{if} \quad \frac{\pi}{2} < \theta \leqq \pi,$$

$$\pi = \pi + \theta \quad \text{if} \quad -\pi \leqq \theta < -\frac{\pi}{2}.$$

The ratio S_θ/S_θ' gives the correction factor for a given angle θ, that is the number by which the measured scattered radiation must be multiplied to give the actual amount scattered. This factor will be too large, however, because, as mentioned above, S_θ' is too small. The diamond splints being the substance requiring the largest correction factor, calculations were made for it for nine values of θ from 0 to π. The factor has its largest value 1.228 at 0 and continuously decreases to its smallest value 1.200 at π, the value 1.216 at $\pi/2$ being almost the mean of the other two.

Now we may get another estimate of the correction factor by assuming that all of the originally scattered radiation which is rescattered gets out. With this assumption the fraction of the original beam getting out of the cylinder per unit solid angle in the direction making an angle θ with the beam is given by the following expression:

$$S_\theta'' = f(\theta)$$

$$\times \int_{-R}^{+R} \int_{-\sqrt{R^2-x^2}}^{+\sqrt{R^2-x^2}} \epsilon^{-\mu\left[x + \sqrt{R^2-y^2} + \sqrt{R^2-(x\sin\theta + y\cos\theta)^2} - x\cos\theta + y\sin\theta\right] - \sigma\sqrt{(R^2-y^2)}+x)} dx dy.$$

Since the previous integral when solved varied so little with the angle θ it was deemed sufficient to solve the above expression for $\theta = 0$. Now

this expression will give too large a value for the scattered radiation getting out of the cylinder, and too small a value for the correction factor for some of the rescattered radiation will be absorbed. The above integral when solved for $\theta = 0$ gives

$$S_\theta'' = f(\theta)\left(1 - \frac{4}{3\pi}\frac{b^2 - a^2}{b - a} + \frac{1}{8}\frac{b^3 - a^3}{b - a} - \frac{4}{45\pi}\frac{b^4 - a^4}{b - a} + \cdots\right),$$

where $a = \mu D$; $b = (\mu + \sigma)D$.

The values of S_θ/S_θ' and S_θ/S_θ'' for $\theta = 0$ for the diamond capsule were respectively 1.228 and 1.130. The mean value of this is 1.179, and since the value 1.228 for $\theta = 0$ was about 1 per cent. larger than the mean value, the value 1.17 was taken as the average correction factor for the diamond capsule. In the case of the other materials the difference between the two estimates of the correction factor were much smaller. For instance for the artificial graphite the two values were 1.11 and 1.07, giving a mean value of 1.09.

The writer takes pleasure in recording the following acknowledgments: To Tiffany and Co. of New York City for lending the diamond splints; to Prof. L. C. Raiford for the mesitylene; to Mr. John R. Couture for the benzene and octane; to Prof. P. A. Bond for the lithium; to Dr. A. W. Hull for the graphite and zirconium-oxide filter used in this investigation; to Mr. J. B. Dempster for much help in the construction and design of the apparatus; to Miss Marcella Lindeman, Mr. Joseph L. Fiala, Mr. Harlan Porter and other students in this laboratory for help in taking observations.

STATE UNIVERSITY OF IOWA,
IOWA CITY, IOWA,
June 9, 1922.

ABSORPTION COEFFICIENTS FOR HOMOGENEOUS X-RAYS.

BY E. G. TAYLOR.

SYNOPSIS.

Absorption Coefficients of Various Organic Liquids for X-rays of Wave-length 0.715 Å.—By means of a spectrometer with narrow lead slits and a calcite crystal, the K_α radiation from the Mo target of a Coolidge tube was reflected into an ionization chamber, and the effect of interposing a cell containing a known thickness of liquid before the first slit, was measured. Thus absorption coefficients were determined for carefully purified samples of *pinene* ($C_{10}H_{16}$), *limonene* ($C_{10}H_{16}$), *benzene* (C_6H_6), *toluol* (C_7H_8), *isopropyl alcohol* (C_3H_8O), *methyl proprionate* ($C_4H_8O_2$), *ethyl acetate* ($C_4H_8O_2$), *acetone* (C_3H_6O), *ethyl formate* ($C_3H_6O_2$) and *trimethylene glycol* ($C_3H_8O_2$).

Atomic absorption coefficients for C, H, and O for X-rays of wave-length 0.715 Å. were computed from the above data, assuming absorption to be an additive atomic property, and came out from 11.00 to 11.55 $\times 10^{-24}$ for C, 0.45 to 0.50 $\times 10^{-24}$ for H and 29.9 to 31.0 $\times 10^{-24}$ for O. Using the mean values, the computed coefficients are within $\frac{1}{2}$ per cent. of the observations, on the average. But the fact that the computed values for acetone and water are 1 per cent. too low suggests that the *assumption that absorption is an atomic property* may not be accurately true.

THIS research was undertaken to obtain new data upon the absorption of x-rays because of the great variation in the results obtained by different investigators. The work of Hull,[1] Richtmyer and Grant,[2] Richtmyer,[3, 4] Hewlett[5] and Bragg[6] has shown that for homogeneous x-rays the absorption is proportional to the cube of the wave-lengths of the incident radiation. This emphasizes the desirability of working with as near pure monochromatic radiation as possible.

In this work the author proceeded first to determine the molecular absorption of several organic compounds. If one assumes an additive relation for molecular absorption it is then possible to determine the atomic absorptions of the constituent elements. In this way the atomic absorption coefficients were determined for hydrogen, carbon and oxygen for the wave-length 0.715 Å.

[1] PHYS. REV., Vol. 8, p. 326, 1916.
[2] PHYS. REV., Vol. 15, p. 547, 1920.
[3] PHYS. REV., Vol. 17, p. 264, 1921.
[4] PHYS. REV., Vol. 18, p. 13, 1921.
[5] PHYS. REV., Vol. 17, p. 284, 1921.
[6] Phys. Mag., Vol. 28, p. 626, 1914.

The molecular absorption is defined as that fraction of the incident radiation which is absorbed per molecule per square centimeter of surface normal to the direction of the pencil of rays. In this work the absorption means the total decrease of the incident radiation which includes the "true absorption" and the scattering effect. The molecular absorption was computed from the mass absorption through the relation,

$$M = \frac{\mu}{\rho} m,$$

where M represents the absorption of the molecule,
m represents the actual mass of the molecule,
μ represents the absorption of substance as determined,
ρ represents the density of substance used.

In this computation the mass of the hydrogen atom has been taken as 1.64×10^{-24} gms.

The hydrocarbons used for the determination of the atomic absorptions of hydrogen and carbon were pinene, limonene, benzene and toluol. The atomic absorptions were then determined from two simultaneous equations involving the molecular absorptions of two different compounds. For example the following equations:

$$10\mu_c + 16\mu_H = 1.209 \times 10^{-22},$$
$$6\mu_c + 6\mu_H = 0.707 \times 10^{-22}.$$

Apply to pinene and benzene respectively, μ_c and μ_H representing the atomic absorptions of carbon and hydrogen and the right members representing the molecular absorptions of the compounds.

Having determined the atomic absorptions of hydrogen and carbon the absorption of the oxygen atom was determined from the molecular absorptions of several organic compounds containing oxygen.

METHOD.

The general method of making these measurements did not involve any essentially new principle. The radiation used was that of the K_α line from a molybdenum-target Coolidge tube. The radiation first passed through two very narrow lead slits which limited the divergence of the beam to a few minutes of angle. The emergent radiation was then incident upon a calcite crystal set at the proper angle to reflect the K_α line in the first order. After reflection the radiation passed through another slit into the ionization chamber.

The central electrode of the ionization chamber was supported in a bakelite insulator and connected to the leaf of a Bumstead electroscope.

Methyl iodide or ethyl bromide was used to increase the ionization. Considerable difficulty was experienced with leakage when the vapor density approached that of saturation. By using an ionization chamber approximately 70 cms. long sufficient ionization was produced when the vapor density was low in which case the leak became negligible or could easily be corrected for. The intensity of radiation was measured by the rate of change of potential of the central electrode as indicated by the electroscope.

The various solutions were held in a small bakelite cell while the absorption determinations were being made. This cell was placed in front of the first slit and in this way scattered radiation was prevented from entering the ionization chamber.

The filament of the tube was maintained at a constant temperature by a set of storage batteries while the potential across the tube was supplied by a 5 KVA high-tension transformer. Since the primary voltage was supplied from the mains small variations of potential across the tube were unavoidable. To make the effect of this variation as small as possible the data were taken in a continuous series of observations lasting over a considerable time. In this way the error due to the fluctuations of potential tended to eliminate itself in the mean of several observations.

The absorption was computed from the following formula,

$$\mu = \frac{2.30}{d} \log_{10} K \frac{T_x}{T_0},$$

where d represents the thickness of the absorber, T_x and T_0 the times required to change the potential of the system to some constant and arbitrary value with and without the absorber and K the fraction of the incident energy transmitted by the empty cell.

RESULTS.

From the data taken the molecular absorption was computed from the relation previously given. The following table gives the results directly obtained from the data for the hydrocarbons.

Compound.	μ.	Molecular Absorption $\times 10^{24}$
Pinene, $C_{10}H_{16}$	0.464	1.209
Limonene, $C_{10}H_{16}$	0.457	1.206
Benzene, C_6H_6	0.485	0.707
Toluol, C_7H_8	0.477	0.834

From these different compounds various sets of simultaneous equations may be written and from them the atomic absorption of carbon can be determined. These values for the absorption of the carbon atom together with the different combinations of the compounds used are as follows:

Benzene—Pinene	0.1132×10^{-22}
Benzene—Limonene	0.1137×10^{-22}
Benzene—Toluol	0.1100×10^{-22}
Toluol—Limonene	0.1155×10^{-22}
Toluol—Pinene	0.1148×10^{-22}
Mean =	0.1134×10^{-22}

Knowing the absorption of the carbon atom it was then possible to get the absorption of the hydrogen atom from the molecular absorption of each of the hydrocarbons used. The values obtained for hydrogen from the different compounds are, pinene 0.0050, limonene 0.0045, benzene 0.0045 and toluol 0.0047. In each case the numerics are multiplied by 10^{-22}.

The results obtained for the atomic absorption of oxygen and the compounds from which they were obtained are given below.

Substance.	μ.	Molecular Absorption.	Atomic Absorption of Oxygen.
Isopropyl Alcohol, C_3H_8O	0.544	0.683×10^{-22}	0.304×10^{-22}
Methyl Proprionate, $C_4H_8O_2$	.698	1.089	0.299
Ethyl Acetate, $C_4H_8O_2$	.684	1.099	0.304
Acetone, C_3H_6O	.563	0.679	0.310
Ethyl Tomate, $C_3H_6O_2$	.737	0.970	0.301
Trimethylene Glycal, $C_3H_8O_2$	.833	0.986	0.304

Mean = 0.304×10^{-22}.

A summary of all results obtained by the author and those obtained by others are included in the following table.

Preliminary experiments showed the necessity of specially prepared chemical compounds to avoid the impurities which are often present in materials supposed to be pure. In the preparation of the hydrocarbons the author commenced with relatively pure samples of pinene, limonene and benzene and further purified these through repeated distillation or crystallization. The toluol used was not further purified but since it gave results in agreement with those obtained from the other compounds the results are likewise included in the tables. The oxygen compounds were specimens very carefully purified by Mr. G. A. Ramsdell of the department of chemistry and left little to be desired in their purity.

Substance.	Observers.			
	Hewlett.	Richtmyer.	Windgårth.	Taylor.
Carbon, μ/ρ	0.551		0.667	
μ_a*	0.1084[2]		0.1313[2]	0.1134
Oxygen, μ/ρ	1.126		1.000	
μ_a	0.295[2]		2.62[2]	0.304
Hydrogen, μ_a	0.011[1]			0.0048
Aluminum, μ/ρ	5.17	5.32	5.28	5.15
μ_a	2.30[2]	2.37[2]	2.36[2]	2.29
Water, μ/ρ	1.073	1.129	1.013[2]	1.089
μ mol.	.317[2]	0.333		0.322
Acetone, μ/ρ			0.786	0.714
μ mol.			.748[2]	0.679

μ_a* Written for atomic absorption.

The high value obtained by Windgårth for the absorption of oxygen is probably due to an impurity of high atomic weight. The molecular absorption of acetone as determined by that investigator is considerably higher than the value obtained by the writer. Acetone and many other organic compounds absorb moisture from the air and unless used soon after preparation will cause an error depending upon the amount absorbed.

From the data it is seen that two pairs of isomers have been used. Within the limit of the experiment the molecular absorptions are the same for the compounds of the same composition and offer additional evidence in favor of the view that x-ray absorption is an atomic property. In the case of oxygen however there seems to be a difference between the atomic absorption of oxygen as determined by Hewlett using liquid oxygen and that determined from oxygen compounds in this investigation which is somewhat greater than the error of measurements. Whether there is any significance to this small difference can only be determined by additional work in which the same investigator uses both forms of oxygen. Some doubt may also be cast upon the belief that x-ray absorption is a property of the atom only when one considers the absorption of hydrogen as determined in this research. From the measurement of the molecular absorptions of four hydrocarbons the atomic absorption of

[1] Computed from author's data on water and oxygen.

[2] Computed from author's data.

[3] Computed from author's data from value for $\lambda = .430$ Å. by the relation $\mu/\rho = K\lambda^3 + \sigma/\rho$.

hydrogen was found to be 0.0048×10^{-22}. When the atomic absorption of oxygen 0.304×10^{-22} is subtracted from the molecular absorption of water, 0.322×10^{-22} a value is found for the absorption of hydrogen approximately twice that as determined from the hydrocarbons. This difference in the absorption of the hydrogen atom seems considerably greater than the experimental error would account for. This apparent difference in the absorption of hydrogen in water and in hydrocarbons might be caused by a difference in the strength of the bond uniting the hydrogen to the other elements of the compound. This seems the most probable when one realizes the extreme stability of the hydrocarbons and the ease with which water is broken up.

UNIVERSITY OF WISCONSIN,
MADISON, WISCONSIN,
Aug. 5, 1922.

A SECOND UNDAMPED WAVE METHOD OF DETERMINING DIELECTRIC CONSTANTS.

BY A. P. CARMAN AND G. T. LORANCE.

SYNOPSIS.

New Undamped Wave Method of Measuring Capacities, Changes of Capacity and Dielectric Constants.—A previously described method is very fatiguing, since it involves adjusting a beat tone produced by two ultra-audion circuits, to the same pitch as that of a standard tuning fork. The new method involves merely reading galvanometer deflections, and depends upon the observation that under certain conditions the *relation between current in plate circuit and capacity in the oscillating circuit* is linear for a limited range, therefore three current readings, corresponding to an unknown and two known capacities, are sufficient to determine the unknown. Small changes of capacity, for instance 0.01 cm. in 1000 cm., can readily be detected and measured. The accuracy of the method is practically equal to that of the standards if sufficient care is taken to keep circuit conditions constant.

Dielectric Constant for Air, Carbon Dioxide and Illuminating Gas.—Preliminary results obtained by the above method are 1.00060, 1.00099 and 1.00077, respectively, for 76 cm. of Hg.

IN December, 1919, W. H. Hyslop and the first named of the present writers, presented a paper before the American Physical Society[1] on "An Undamped Wave Method of Determining Dielectric Constants of Liquids." This method uses two circuits of the "ultra-audion" type, one operating at a constant frequency, and the other tuned by changing the capacity of an adjustable condenser to such a frequency that a definite beat tone is obtained for the two circuits. The beat tone is fixed by the ear, a tuning fork being used as a standard for comparison. A substitution method is then used to determine the capacity of the condenser with and without the dielectric. Later, Professor Whiddington[2] published the account of his ingenious use of ultra-audion circuits to measure minute changes in distance between air-condenser plates by the changes in capacity. Other uses of the same general method have since been independently made.

Recent work carried on by the first writer and his students has shown that while the limit of accuracy of the above ultra-audion method is theoretically only that of the calibration of the adjustable capacity standards, yet practically there is a limit owing to the fatigue of the ear. After an observer has worked a half-hour or so in tuning a circuit with a tuning fork or other tone standard, he is apt to become fatigued and

[1] PHYS. REV., Vol. XV., p. 243, 1920.

[2] Phil. Mag., Nov., 1920.

nervous. While we have considerable unpublished data on dielectric constants, determined by the above method, we have on account of this fatigue turned attention to developing a method involving the reading of an instrument rather than the one involving the comparison of tones. The method described below was suggested by Mr. J. J. Dowling's "Recording Ultra-Micrometer," [1] and has proved sensitive and convenient in use. One arrangement of the circuit used by us is shown in Fig. 1. There is an audion, with an inductance L and capacity $(C_1 + C_2)$ in the grid circuit arranged so as to generate undamped oscillations of any desired frequency. In the plate circuit, there is joined in parallel

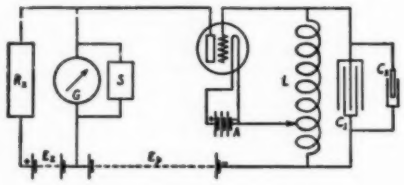

Fig. 1.

the adjustable resistance R_z and the galvanometer G. The resistance circuit R_z includes a battery of e.m.f. E_z, and forms what Mr. Dowling calls a "zero shunt," enabling the use of a sensitive mirror galvanometer G to measure changes in the plate current, when R_z is large compared with the galvanometer resistance. We have used a Leeds and Northrup mirror galvanometer with a sensitiveness of 2×10^{-9} amp. per scale division. A number of curves showing the change of mean plate current with changes of the capacity $(C_1 + C_2)$ were drawn. These curves varied for different voltages E_p in the plate circuit and with the degree of coupling. The curve shown in Fig. 2 is the curve with 50 volts in the

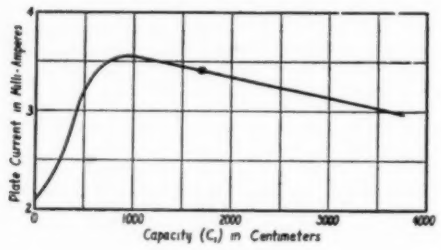

Fig. 2.

plate circuit, and the coupling which was found to give the maximum slope at that voltage. It is noted from this that for capacities from 1,000 to 3,500 cm. there is a linear relation between the mean plate current and

[1] *London Engineering*, Sept. 9, 1921.

the capacity, and a change of 1 cm. corresponds to a change of plate current of 2.1×10^{-7} amperes. It is thus possible to read with the above arrangement a change of capacity of a hundredth of a centimeter. This sensitiveness can be increased by using other e.m.f. of the plate battery and also by using a more sensitive galvanometer, but the above is far more sensitive than called for by the present calibration of our small capacities.

The above method has been tested in the determinations of the dielectric constants of a number of gases. Two "air" condensers were used, the larger one C_1 of a fixed capacity of 3,580 cm. and the smaller one C_2 of adjustable capacity. The construction of these condensers is most easily given by Figs. 3 and 4. The larger condenser is placed in a glass

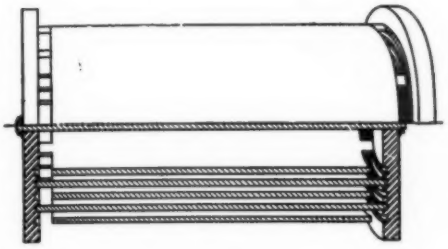

Fig. 3.

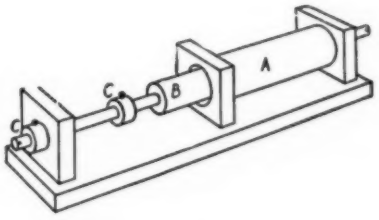

Fig. 4.

cylinder which is exhausted by a "Hy-Vac" pump, and into which the different gases can be introduced. The whole apparatus is enclosed in grounded wire cages. The eyepiece of the galvanometer projects through a small opening in the wire screen. The capacity of the small adjustable cylindrical condenser is changed from the outside by strings. The function of this condenser is to determine the relation between the galvanometer deflections and the change in capacity. The change in capacity of the "air" condenser in a vacuum and with a given gas as dielectric can thus be measured in terms of deflections of the galvanometer. The results which we have obtained are only preliminary since we have not yet calibrated our small standard condenser with the desired accuracy. We are also not sure of the purity of the gases used, though they are from standard producers, and are supposed to be "pure."

Some of the preliminary results are as follows:

TABLE.

Dielectric Constant K for Air.

Change in Pressure in Cms. Hg.	Galv. Deflection for Corresponding Change in C_1.	Galv. Deflection for Calibrating Condenser C_2, Set for 1.5 Cms.	K for 76 Cm. Hg.
0 to 75.....	3.32	3.00	1.000618
0 to 75.....	3.20	2.85	1.000627
0 to 75.....	3.30	3.20	1.000576
0 to 75.....	3.50	3.35	1.000583
Mean.....			1.000601

K for illuminating gas at 76 cm. Hg. = 1.000772
K for carbon dioxide at 76 cm. Hg. = 1.00099

The method is so sensitive that any lack of constancy in conditions becomes important. Thus, one of the greatest difficulties was that of maintaining a constancy of the filament current; as a change of temperature of bulb or other part of circuit, or little irregular action of the storage battery changed the filament current and this showed in the mirror galvanometer in the plate circuit. Most of these minor but important difficulties are now reduced or eliminated.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
URBANA, ILLINOIS,
June, 1922.

ON A NEW METHOD FOR THE GENERATION OF SOUND-WAVES.[1]

BY JUL. HARTMANN,

Dr. techn. Docent in the Royal Technical College, Copenhagen.

SYNOPSIS.

Pressure variation along a high-velocity air jet, produced by a pressure of 0.9 to 5 atm. above normal, was determined with a simple Pitot tube, and the periodic intervals of instability were located (Figs. 2 and 5).

New Source of Sound; Resonator Actuated by a High-Velocity Air Jet.—It was found that the intervals of instability referred to above can be used for the generation of sound. (1) *Bulb form.* When the small orifice to a bulb is placed in one of these intervals so that the particles of air move in and out of the opening, pulsations like those of a siren are produced, the tones not being pure. The fundamental frequency depends on the volume of the bulb, the size of the orifice and the position in the jet, and may readily be varied from 1/10 to 5,000 per second. (2) *Cylindrical form.* When a simple cylindrical resonator is placed with one end in an interval of instability, pure tones are produced except in certain positions when overtones may be present. The frequency is the fundamental of the resonator and may be made as high as 125,000 per second by using a very short tube, about 0.5 mm. in length and in bore. With a hydrogen jet, the frequencies are, of course, 3.8 times as high. The *efficiency* of such sources is remarkable, intensities that are painful being readily produced. Practical forms of these generators are illustrated (Figs. 3 and 4).

INTRODUCTION.

IF air is allowed to stream from a container in which the absolute pressure is more than 1.9 atm.—that is the overpressure is higher than 0.9 atm.—through a hole or a short bore out into the free atmosphere, a jet is produced which exhibits a peculiar periodic structure. It was *Mach* and *Salcher*[2] who first noticed this structure by photographing the jet. Mach explained it as due to stationary sound-waves and suggested an explanation as to how the waves were created. Later the jet was studied by R. Emden[3]—also by means of photography—and he produced a theory for the sound-waves. A direct investigation of the distribution of the pressure in the air-jet was carried out by Parenty[4] by means of a sound which was introduced into the jet, and the same method, but with considerably improved apparatus, was employed by

[1] Extract from "Det kgl. Danske Videnskabernes Selskab. Mathm. fysiske Meddelelser," I., 13, 1919.

[2] Wied. Ann., 41, p. 144, 1890.

[3] Wied. Ann., 69, p. 264 and 426, 1899.

[4] Ann. Chem. Phys., 12, 289, 1897.

Stodola.[1] Stodola's experiments have to a high degree contributed to elucidate the structure of the air-jet. Finally should be mentioned very important work done by Prandtl[2] who succeeded in solving the differential equation for the wave-motion in the jet, and to whom we owe a series of exceedingly instructive photographs of the jet. Thus we now possess a fairly complete comprehension of the air-jet and especially it is now known that the periodical structure is closely connected with the fact of the velocity of the jet, with sufficiently high overpressure, being higher than that of the sound.

THE USE OF THE AIR-JET FOR THE GENERATION OF SOUND-WAVES.

The author has carried out a series of investigations on the jet by means of the arrangement shown in Fig. 1. In this figure, the jet-forming

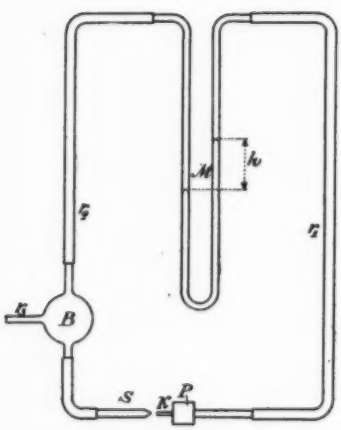

Fig. 1.

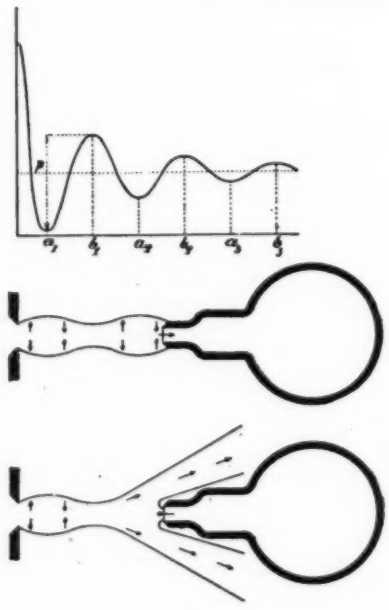

Fig. 2.

element is indicated by the letter S and is shown as a drawn-out glass tube. K designates the sound of a Pitot apparatus connected through the rubber tube r_1 with one of the branches of the U-shaped manometer M. The other branch of M was, through r_2, connected with the bulb B, from which the air was flowing to S. In B the air was kept at a constant pressure by means of a compressor, which through r_3 communicated with B. In the experiment an air-chamber of about $15l$ was inserted between the bulb B, which had a volume of about $\frac{1}{2}l$, and the compressor.

[1] A. Stodola, Die Dampfturbine, Berlin, 1910.

[2] Phys. Zs., 5, p. 599, 1904, and 8, 23, 1907.

In representing the pressure difference h, read on the manometer, graphically for varying positions of the sound K out along the axis of the air-jet one gets a curve of the character shown in Fig. 2, *a*, provided the pressure in B is lying between the above-mentioned critical and a certain higher value. The curve, as will be seen, gives a picture of the periodical structure of the jet. In comparing the curve with photographs of the jet it is found that the Pitot curve fairly truly represents the pressure-variations along the axis of the jet.

It was now found that the intervals $a_1\ b_1$, $a_2\ b_2$, $a_3\ b_3$ and so on, the intervals of instability as they are termed below, within which the pressure increases, may be used for the production of air-waves of two different types, which will be considered separately in the following. For the production of the one kind of waves a bulb, Fig. 2*b*, provided with a tube which is drawn out to a fine aperture, can be used. When this aperture is introduced into one of the intervals of instability, as indicated in the figure where the jet is drawn in correct position to the curve in Fig. 2, *a*, the bulb will periodically fill with, and again exhaust air. The motion of the air particles during the filling and the exhaust is schematically indicated in Fig. 2, *b* and Fig. 2, *c*. The period of the phenomena depends on the size of the bulb, on the width of its mouth, on the position of this latter in the interval $a\ b$, and finally on the interval of instability, and on the pressure in that container from which the air flows to the jet. The larger the volume or the smaller the mouth, the longer the period. All periods from, say, 10 sec. or more to 1/5,000 sec. or less can easily be produced. The rapid oscillations of the air are of course heard as a tone. Same has the same unclear character as that of a siren. We shall in the following term the indicated air-oscillations as *pulsations* in order to distinguish them from the other kind of oscillations which may appropriately be called resonance-oscillations. The latter receive their designation from the fact that they are produced by introducing the mouth of a simple cylindrical resonator (oscillator) into one of the intervals of instability. The air will in this case oscillate mainly with the natural frequency of the resonator so that the produced regular sound-waves attain a wave-length of fully four times the depth of the resonator. Thus the frequency is now to a certain degree independent of the interval of instability as well as of the location of the aperture of the resonator in this latter, and of the pressure of the outflowing air, etc. The intensity of the oscillations however undoubtedly increases with the rise of pressure p in the interval of instability. (See Fig. 2, *a*.) It is ordinarily very high due undoubtedly partly to the high density of the energy in the air-jet, partly to a comparatively very high

efficiency of the generator. (Provisory measurements seem to prove that the efficiency at about 20,000 periods per sec. is as high as 10 per cent.) As to the frequency, resonance-oscillations, *i.e.*, pure acoustic oscillations of 100,000 periods per second or more, can easily be produced by means of a jet of atmospheric air. With a jet of hydrogen a frequency of more than 300,000 can be obtained. As a matter of fact the author has been able to produce intense sound-waves of 340,000 periods, and in all probability there will be nothing to prevent the production of still higher frequencies. The author therefore holds the opinion that the air-jet in connection with a resonator furnishes a means for producing intensive, pure acoustic oscillations of higher frequencies than has hitherto been possible.

PRACTICAL FORMS OF THE ACOUSTIC GENERATOR.

As to the practical construction of an apparatus for the production of air-waves (pulsations of resonance-oscillations) according to the new principle, numerous possibilities present themselves. What is required is merely a means for inserting the aperture of the resonator or "pulsator" (Fig. 2, *b*) into the interval of instability and to center the aperture in relation to the jet. Fig. 3 shows a construction which is adaptable for

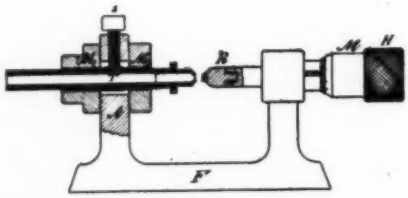

Fig. 3.

many purposes. The pressure-tube is here T, which has been extended with the jet-forming element S. T is carried through the wide bore in the vertical arm A which is provided with plane sides. By means of two nuts M_1 and M_2, T is fastened to A. By loosening one of these nuts the jet-hole may be centered relative to the mouth of the resonator R by means of three screws s_1, s_2, s_3, of which only one, s_1, is shown in the figure. The resonator is made as a cylindrical bore, of approximately the same diameter as the jet-hole, at the end of a short piece of metal. The edges of the bore are sharpened as shown in the figure. The resonator, respectively the pulsator is screwed into the end of the micrometer screw M and can by means of this be adjusted in one or the other of the above-mentioned intervals of instability of the jet. The screw and the

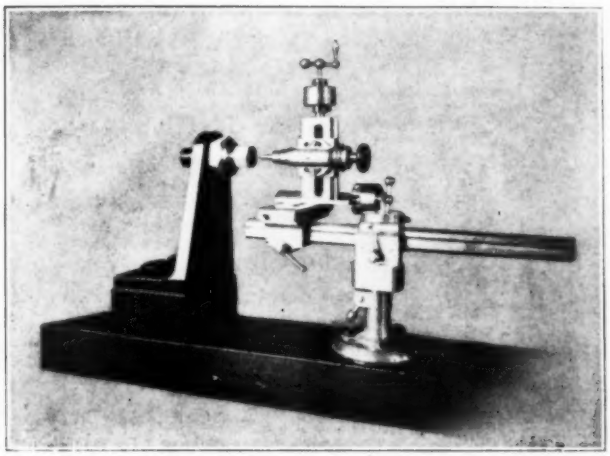

Fig. 4.

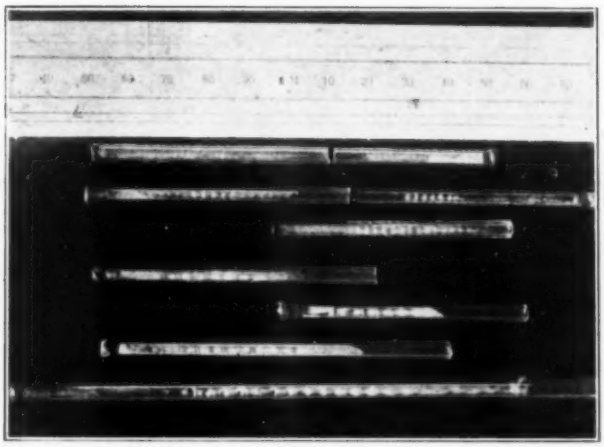

Fig. 7.

JULIUS HARTMANN.

pressure-tube are connected through the baseplate *F* which, if desired, may be attached to a heavier plate or to the apparatus in connection with which the acoustic generator is to be used.

During the fundamental experiments an apparatus was used which has in many respects proved practical. It is shown in Fig. 4. On a heavy iron beam is mounted a vertical stand through which is carried a short pipe. The pipe is at the one end provided with a head into which the jet-forming element is screwed. Another stand on the iron beam carries a horizontal guide rail. On this a combination of three slides may be moved towards or away from the jet-hole. The one slide carries a small chuck in which the resonator can be fastened. By means of two of the slides the resonator can be centered in relation to the jet. By means of the third one the aperture of the resonator can be carried into the interval of instability. Well suited for the jet-forming element is a glass tube drawn out to a short point. Equally suited is a conical bore in a metal plate and this latter form is of course easier to produce. Cylindrical bores are less satisfactory even if they have a conical inlet, as a certain pressure is lost in such bores.

In the event of no compressed-air plant being available, the air for the acoustic generator is taken from a compressed-air bottle. The bottle must of course be provided with a reduction valve. Between this and the generator is preferably inserted an air chamber of a capacity of some liters and provided with a valve by means of which the air supply to the generator may be stopped.

EXPERIMENTS ON THE LOCATION OF THE INTERVALS OF INSTABILITY.

In the following an extract will be given of the experiments, which were carried out as a basis for the new acoustic generator. Fig. 6 represents a curve showing the variation in the readings of the manometer in Fig. 1 out along the axis of an air-jet produced by an over-pressure of 141.0 cm. mercury and by a jet-hole of 0.535 mm. The distances from the jet-hole, measured on a scale, were 100 divisions are equal to 0.275 mm., are shown as abscissæ, and as in Fig. 2, the ordinates represent the difference between the pressure in the container and in the jet. The great regularity in the periodical pressure-variations is especially to be remarked. The approximate location of the intervals of instability is shown in the figure. The second interval extends somewhat out over the pressure-maximum, this is however only due to the uncertainty in the determination of the location. The extension of the intervals of instability was found by means of small "pulsators" made of glass tubes which were at the one end drawn out to a small aperture and at

the other end closed by sealing-wax. In the examination of the first interval in Fig. 5, two pulsators of different sizes were used. Each of

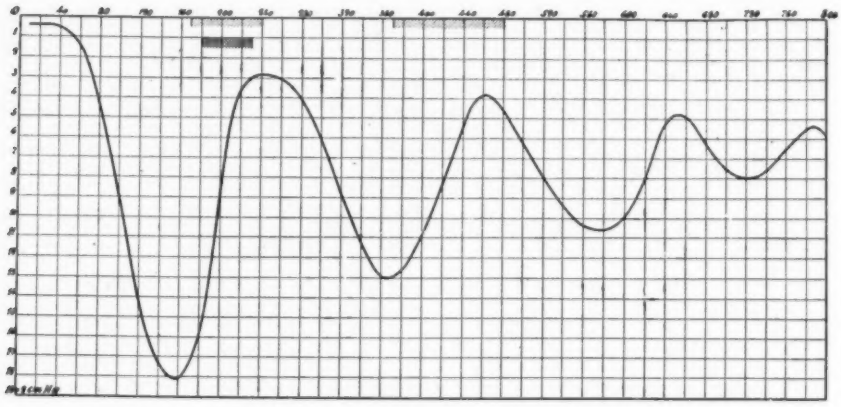

Fig. 5.

the two indicated intervals corresponds to its pulsators. The largest interval was found by means of the largest pulsator. The smallest pulsator had a volume of only some few mm.^{3}, the largest was not larger than that its pulsations could be heard as a tone. If the aperture of the

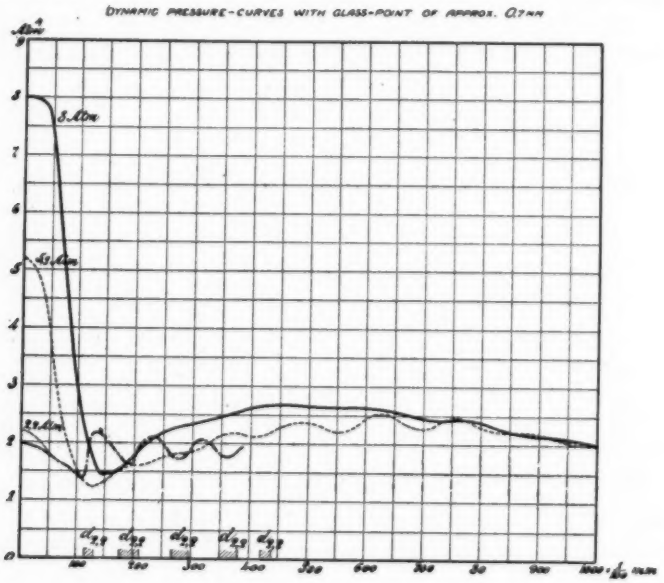

Fig. 6.

smallest pulsator was placed in the first part of the first interval (nearest the jet-hole) it would produce, within the small interval which is denoted in the figure by a double-arrow, a pure tone of about 100,000 oscillations per second.

The periodical character of the pressure-variations in the jet is only observed for overpressures under a certain limit. Fig. 6 illustrates the changes when this limit is passed. At the lowest overpressure of 2.2 atm., the periodical pressure-variations and the sharply separated intervals of instability $d_{2.2}$, $d_{2.2}$, $\cdots$ again occur. Altogether five such intervals have been observed. Undue importance must not be attached to the limits of the intervals, as the determination of same was connected with great uncertainty. When the pressure is increased the intervals by and by are mingled up. At a pressure of 5.2 atm., an interval of

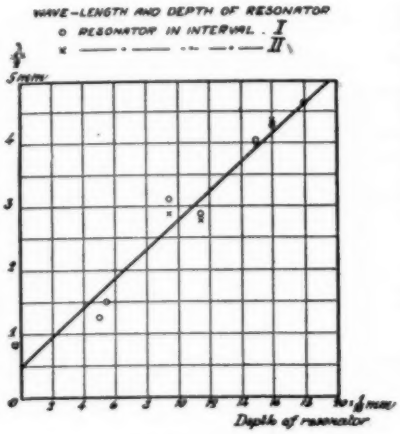

Fig. 8.

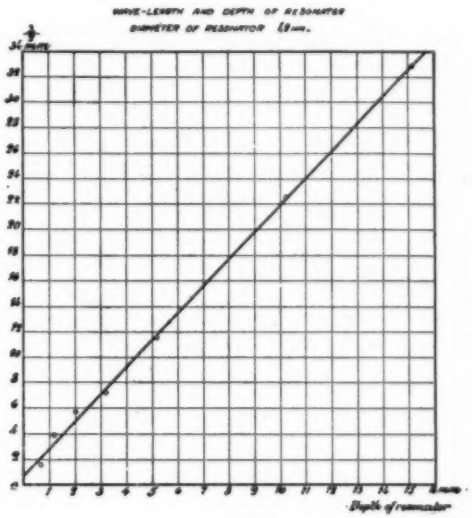

Fig. 9.

instability started at the abscissa 350 and extended to 620. Thereafter followed a smaller isolated interval from 660 to 700. With a resonator (No. 13) which produced a rather high tone, the beginning of the interval of instability was observed as low as 230 and the interval extended to about 900. Possibly there could be traced outside this interval a smaller one between 950 and 1050.

Experiments on the Dependency of the Number of Oscillations on the Dimensions of the Resonator.

A number of resonators of the type shown in Fig. 3 were produced. The depth d was measured and it was investigated how the produced oscillations depended on d. The wave-length λ corresponding to the oscillations was measured by means of Kundt-tubes. Samples of the dust-figures are shown in Fig. 7 together with a millimeter scale which makes it possible to determine the length of the waves. In Fig. 8 a curve is reproduced showing the variation of $\lambda/2$ with d, for a number of

very small resonators, all of which had an aperture of 0.7 mm. The two series of observations correspond to the two first intervals of instability. The curve is, as will be seen, a straight line. In Fig. 9 are represented the results of a second experiment which was made with deeper resonators of 1.2 mm. aperture. The curve is also here a straight line and may with the units of the figures be represented by the formula:

$$\lambda = 4.22 \cdot d + 1.2,$$
$$\lambda = 4.22\ (d + 0.3).$$

The wave-length is thus, as may be expected, approximately 4 times the depth of the resonator. The divergence from 4 is perhaps due to the fact that the temperature of the oscillating air in the resonator is not the same as that in the Kundt-tube. The constant 1.2 in the first formula indicates the well-known fact that the oscillations in the resonator extend somewhat outside the mouth of the resonator. It is usually assumed that the extension outside the mouth is approximately 0.6 time the radius of the resonator. In the second formula 0.3 should represent this extension in fairly good accordance with that assumed, 0.6 time the radius of the resonator 0.6 being 0.36.

The frequency of the oscillations of the resonator is as already mentioned, mainly determined by the dimensions of the resonator, and especially by its depth. Hereby it is of course assumed that the resonator is always blown with the same kind of air. If a jet of hydrogen is used, the frequency is found to be, as is to be expected and as has already been indicated, about four times as high as with a jet of atmospheric air. For instance the following results were found:

Resonator.	λ/2 Air.	λ/2 Hydrogen.	Proportion.	Remarks.
6.....	0.464 cm.	0.130 cm.	3.6	
8.....	0.145 cm.	0.050 cm.	3.0	uncertain
14.....	3.47 cm.	0.925 cm.	3.5	

The proportion between the wave-lengths (measured in the same medium) should be 3.8. If it is perhaps somewhat lower, it may be because the technical hydrogen used was not quite pure.

The intensity of the here-considered resonance-oscillations is, as already stated, very large, notwithstanding the smallness of the resonator. The possibility of making the resonator very small, especially of a small diameter, explains how it comes that the frequency can be made as high as is actually the case. A small diameter means a small value of the constant term in the formula for the wave-length. Now it is obvious

that the smaller this term is the smaller values or the higher frequencies can be obtained by diminishing the depth d of the resonator. By way of illustration we may consider a resonator of a depth 0.5 mm. With such a resonator the diameter can at least be made as small as 0.5 mm. The constant term will in this case be

$$\frac{0.6 \cdot 0.5}{2} = 0{,}15 \text{ mm.}$$

Thus the effective depth of the resonator is 0.65 mm. which gives

$$\frac{320{,}000}{4.065} = 123{,}000 \text{ periods per sec.,}$$

the velocity of sound being 320,000 mm./sec. With a hydrogen-jet the frequency would be $3.8 \cdot 123{,}000 = 476{,}000$ periods per sec., thus very nearly half a million per sec. It may be remarked that oscillations of very high frequencies can easily be produced as first overtones of oscillators of greater depth. Some observations are stated in the table below. The first overtone is produced by adjusting the aperture of the resonator right up to that limit of the first interval of instability which is nearest to the jet-hole. In the indicated experiments the highest frequency is, as will be seen, about 120,000 periods per sec.

Resonator.	λ/2 Fundamental Note.	λ/2 Overtone.	Proportion.
22.....	1.20 mm.	0.400 mm.	3.0
7.....	0.65 mm.	0.205 mm.	3.2
12.....	0.49 mm.	0.142 mm.	3.4

The intensity of the resonance-oscillations may be illustrated by the following example. A resonator of about 24,000 periods per sec. and with an aperture of 1.7 mm., was adjusted in an air-jet produced with a bore of 1.5 mm. With an overpressure of 4–5 atm. very good dust-figures were obtained at a distance of about ½ m. from the resonator when a Kundt tube of 4 mm. aperture was used. With a resonator of about 10,000 periods per sec. and with an aperture of 1.5 mm. the produced tone was even with rather small overpressures almost unbearably intensive and left the observer with a physiological after-effect of several hours' duration.

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ON THE INFLUENCE OF THE SURFACE-TENSION ON THE EFFLUX OF A LIQUID IN JET FORM.[1]

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SYNOPSIS.

Influence of Surface Tension on the Efflux of a Liquid Jet.—Christiansen suggested that surface tension exerts a pressure acting against the pressure causing the flow, so that the Torricelli equation becomes: $v^2 = 2\pi^2\kappa^4\gamma^4 g(h - h_0)$. If then κ, the coefficient of effective contraction, is constant, v^2 should be a linear function of h, intercepting the $h = 0$ axis at h_0. *Experiments with mercury and water*, in which the speed of efflux was determined down to low values of h, confirm this theory. With cylindrical holes, straight lines were obtained, but with conical holes the relation is curvilinear because of the decrease of the contraction with the speed; yet both types of curve gave the same value of h_0. With water, holes through paraffin paper were used. When the speed decreased to a critical value for each jet, pulsations began to appear but these did not affect the speed of efflux. Photographs are given of various jets. As a qualitative confirmation of the theory, ether vapor, which is known to decrease the surface tension of water, was found to decrease h_0 by 18 per cent.

Jet Method of Measuring Surface Tension.—According to Christiansen the surface tension is equal to $r\rho g h_0$. The measurements with mercury and water confirmed this relation, as after correcting for the loss of head in the cylindrical hole, the values of the surface tension came out 536 dynes/cm. for Hg at 16° C. and 74 dynes/cm. for water at 10° C., within one per cent. of the accepted values. It is believed the method is capable of higher accuracy, if developed.

INTRODUCTORY.

AN influence of the surface-tension on the efflux of a liquid in jet form has long ago been recognized. But the manner in which the tension acts has very often been highly misunderstood. Thus, when, from a certain orifice at a certain head, there flows per sec. a greater volume of a liquid with a smaller surface-tension than of a liquid with a larger one, this fact has been accounted for by the supposition of the surface-tension in the latter case tightening the jet to a greater extent and thereby increasing the contraction. For instance this explanation will be found in Jamins's textbook, Cours de Physique, Vol. I. Possibly it has from there or from the source used by Jamins found its way into other textbooks. I give Jamins's representation of the matter:

"*Girard*[2] avait déjà constaté que l'alcool coule plus rapidement que

[1] Extract from the report in Det kgl. Danske Vidensk. Selsk. Math.-fysiske Meddelelser' II., 8, 1919.

[2] Girard, Mémoires de l'Académie, T. I., 1816.

l'eau à travers des orifices percés en mince paroi: la section contractée de la veine doit donc être plus grande pour l'alcool que pour l'eau, et c'est en particulier ce qui résult de mesures directes de *M. Isarn*.[1] Il suffit, d'après ce dernier savant, de vaporiser de l'alcool ou de l'éther à peu de distance d'un orifice par lequel l'eau s'écoule, pour que, le liquide à faible tension superficielle se disolvant dans l'eau, la dépense de l'orifice augmente dans une proportion apprèciable."

Probably the first to propound the explanation which according to the investigation described in the following is the true one, is the late Professor C. Christiansen.[1] The surface-tension being C, there must, in the opinion of Professor C. Christiansen, exist, in a cylindrical jet with radius r, a pressure C/r which counteracts the efflux and which must be subtracted from the pressure under which the liquid flows out, when on the basis of Torricelli's principle it is desired to calculate the quantity of liquid leaving the orifice. Professor C. Christiansen endeavored to carry through the investigation which has now been executed by me, but his attempt was unsuccessful and indeed the result could not well be otherwise in view of the imperfect apparatus utilized. The author took up the experiments mainly because they promised a simple method for the measurement of surface-tensions and because it could not a priori be taken for granted that Professor Christiansen's view of the influence of the tension was incontrovertibly correct. The result has been a complete verification of Professor Christiansen's hypothesis in that the determination, on basis of same, of the surface-tension for water and mercury has given values for these physical constants practically consistent with the best hitherto obtained. After having substantiated this the author has, on basis of the experiments, worked out a new method for the determination of the surface-tension.

RESEARCH APPARATUS.

The research apparatus shown in Fig. 1, *a–c*, consisted of a cylindrical cast-iron basin with an inside diameter of 14.845 cm. and a depth of about 9.5 cm. On opposite sides of the basin were placed two stiffenings, F, with plane outsides. Through each of these and the wall of the cylinder two bores were carried, Fig. 1, *c*. One of these in each stiffening was intended for a window, V. In the second bore in one of the stiffenings the jet-forming element P—the hole-plate—was screwed. The corresponding bore in the second stiffening was not utilized and was therefore closed by a plug.

In the experiments it is necessary to be able to open and close the

[1] C. Christiansen, Ann. d. Phys., 5, 436, 1901.

jet-hole rapidly. The lock is shown in Fig. 1, *a*; it was fixed on the plane front of the stiffening *F'*. From *F'* it was insulated electrically by means of the fiber disc *I*. To this the short horizontal arm A_1 was attached. To A_1 again the vertical arm A_2 could be fixed by means of the screw *K*, so that the arm and what was attached to it could easily be removed when

Fig. 1 *a*.

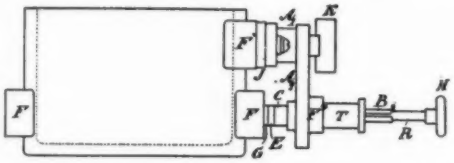


Fig. 1 *b*.

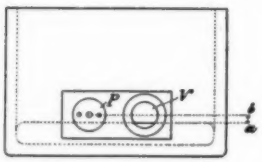
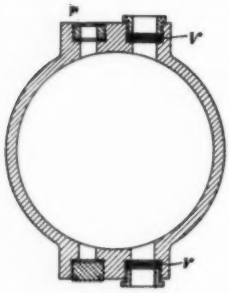


Fig. 1 *c*.



the hole-plate had to be changed. A_2 had below a stiffening *F''*, in which the lock itself could be moved to and fro and fixed in an appropriate position. The lock consisted of a steel disc *E* at the end of the solid cylinder *C*. The edge of *E* was provided with a plain rubber ring, fitting into a groove cut in *E*. When the lock was shut the ring was pressed against the plane foreside of the jet-hole plate. The pressure was exerted by a strong spring placed inside the hollow cylinder *T*. The drawing of the rod *R* outwards, by means of a handle, *H*, opens for the liquid. By means of the bayonet arrangement *B* the lock device, after having been drawn out, could be kept open. Finally it could be closed by a short turn of the handle *H*.

The reason why the lock has been insulated from the basin was that, in other experiments, not dealt with in this paper, it was necessary to transmit an electric current through the jet The disc *E* thereby was to serve as one of the electrodes. The apparatus described was used in the following manner. In the basin was poured 250 cm.^{3} of the liquid

with which the experiment was to be carried out. The surface of the liquid formed a bottom in the basin and the depth of this bottom below the center of the jet-hole was measured by a cathetometer with an accuracy of about 0.05 mm. After this a further 1250 cm³. of the liquid was poured into the basin. The inside diameter of the latter having been measured—also by the cathetometer—the head of the surface of the liquid above the center of the jet-hole could be calculated. The experiment of efflux now consisted in the observation—by means of a stop-watch—of the time of efflux for a series of equal volumes—50.2 cm.³—of the liquid. Of these observations the values of the volume V which flowed out per second were calculated and were written in a table together with the corresponding values of the head. The latter had been calculated once for all under the supposition that each of the tapped-out portions was 50.2 cm.³ and furthermore under the assumption that the center of the jet-hole was situated 0.185 cm. above the liquid bottom. If the latter height had a different value a correction was introduced for the "zero error." On the other hand no correction was used for the small oscillating deviations from the value 50.2 cm.³ of the tapped-out portions. The average heads were calculated as the simple means of the heads of the surface before and after the efflux of the corresponding liquid portion. The error hereby committed is given by the expression

$$\Delta h = \frac{h_1 + h_2 - 2\sqrt{h_1 h_2}}{4}$$

h_1 resp. h_2 being the effective heads before and after. However in practically every case this error could be ignored. The table finally was reproduced in a $V^2 - h$ curve, *i.e.*, a curve which for abscissæ has the head h, for ordinates the square V^2 of the liquid volumes emitted per second. The head corresponding to the counterpressure of the surface-tension being denoted by h_0, the value of V given by Torricelli's law will be

$$V = \frac{\pi}{4} \kappa^2 \cdot d^2 \cdot \sqrt{2g(h - h_0)},$$

κ being the *coefficient of efflux* or the *coefficient of the effective contraction* and d being the diameter of the jet-hole. Thus the equation of the $V^2 - h$ curve should be

$$V^2 = \left(\frac{\pi}{4} \kappa^2 d^2\right)^2 \cdot 2g \cdot (h - h_0)$$

and so, if κ is a constant, the $V^2 - h$ curve should turn out to be a straight line, which if the h-axis cuts off the length h_0 of which the surface-tension

C, according to Professor Christiansen, can be calculated by the expression

$$h_0 = \frac{2C}{d'\rho g},$$

d' denoting the diameter of the jet and ρ the density of the liquid.

A. Experiments with Mercury.

Alternations in the Aspect of the Jet During the Efflux.

As the surface sinks in the basin during the experiment of efflux the jet of course declines more and more. At the same time its surface will—as long as the head of the liquid still remains above a certain limit—appear more and more smooth. Towards the end of the efflux the jet assumes an aspect, which to some degree depends on the diameter of the jet-hole. With wider bores, for instance bores of 2 mm. and upward, the jet continues to be smooth, and forms, almost to the moment when its velocity is nought, a continuous jet of several cm. length. Fig. 2, *a*, shows a photograph of such a jet produced by means of a jet-hole in carton of 1.96 mm. thickness. Immediately before the cessation of the efflux the long jet suddenly becomes unstable and the efflux hereafter takes place in a marked pulsating manner, the jet which is now quite short assuming a glimmering aspect. With somewhat narrower bores—for instance of 1.2 mm.—the instability occurs at a greater head. With bores of a diameter of about 1.4 mm. a peculiar phenomenon may be observed, the jet changing suddenly from the smooth to the pulsating form and later on reverting to the smooth again. Fig. 2 *b*, shows a photograph of a "jet" of 1.432 mm. during the pulsating efflux. With very narrow bores of a fraction of a millimeter the pulsating form of efflux becomes extremely marked, the mercury ultimately trickling from the jet-hole in small drops.

Fig. 2 *a*. Fig. 2 *b*.

It appears from the investigation that the $V^2 - h$ curve with cylindrical bores is rectilinear down to the smallest heads. The transition from smooth to pulsating jet does not alter the direction of the line essentially but if the efflux takes the form of drops this is easily seen from the $V^2 - h$ curve as Fig. 3 will illustrate. The average pressure, due to the

surface tension inside the mercury drops, being smaller than the corresponding pressure inside a jet with a diameter equal to that of the bore, more mercury will flow out in the case of drops than in the case of a jet.

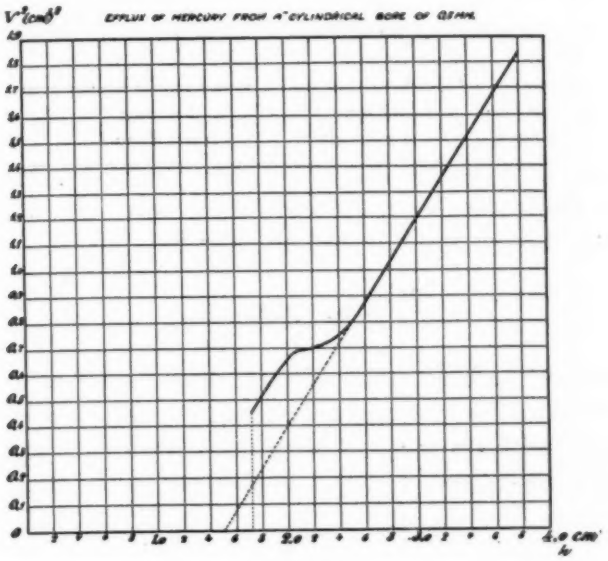


Fig. 3.

Therefore when the phase of drops commences, the $V^2 - h$ curve will to begin with take an upward bend, thereafter falling smoothly owing to the diminishing head.

The Cessation of the Efflux.

When the head has reached a certain lower limit the efflux suddenly ceases and the mercury in the jet-hole will assume a curved surface as shown in Fig. 4. The tension in this surface now supports the remaining mercury-column h_0'. Determinations of h_0' were made for a series of bores, partly of the conical, partly of the cylindrical type, and it was found that the certainty of the measurement of h_0' was very considerable. By way of illustration the following repeated values of the last tapped-out portion in four experiments, carried out with the jet-holes indicated over each of the four last columns, are given below.

Fig. 4.

In the experiments the last portion after having been measured was poured back into the basin for a new measurement. The uncertainty seems to be abnormally great in the second experiment and yet it is here as low as 3 cm.^{3}. This means that the head at which the efflux ceases is determined by one single observation with a certainty of about 0.16 mm. In the other experiments the certainty is essentially greater.

No.	0.80. 90°	0.93. 90°	2.0. 90°	1.5 cyl.
1.....	9.2 cm.³	43.5 cm.³	1.7 cm.³	7.8 cm.³
2.....	8.5	40.1	1.7	6.7
3.....	8.2	42.5	1.9	6.7
4.....	8.8	45.0	1.6	—
5.....	—	—	2.1	—
Mean .	8.7 cm.³ $\Delta=0.5$ cm.³	42.8 cm.³ $\Delta=2.7$ cm.³	1.8 cm.³ $\Delta=0.2$ cm.³	7.1 cm.³ $\Delta=0.7$ cm.³

Provided the surface of the liquid in the bore, Fig. 4, is spherical with a radius of curvature r', r' will be given by

$$\frac{2C}{r'} = h_0' \cdot 13.55 \cdot 981,$$

C indicating the surface-tension of mercury. Assuming r' to be proportional to the radius r of the bore so that $r' = kr$, then in tracing the variation of h_0' with $1/r$ or $1/d$, d being the diameter of the jet-hole, one should get a straight line. In Fig. 5 all observed values of h_0' are marked

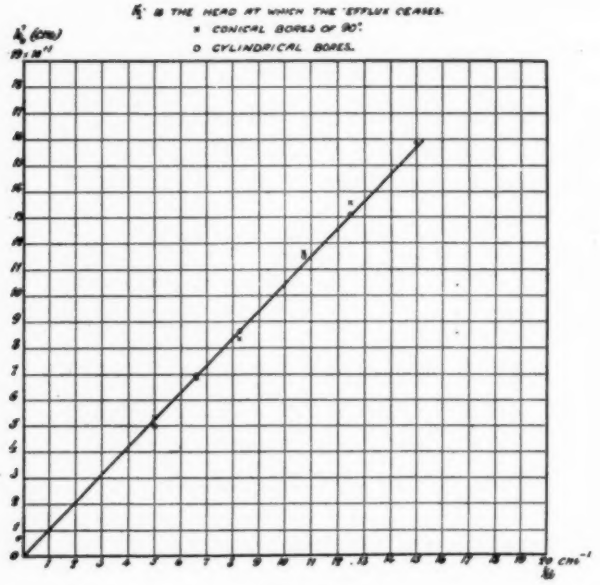


Fig. 5.

in their dependency on $1/d$. Ignoring the value corresponding to the bore with the diameter 0.53 mm., which bore also showed anomalism, with regard to the conditions of efflux, considered above, all the points of observation are distributed with great regularity on both sides of a

straight line through zero. From this line one derives for the constant k the value 1.496, when the value 520 dyn./cm. is used for C. *Thus mercury assumes in the jet-hole a radius of curvature which with a fair degree of accuracy is equal to* 1/50 *times the radius of the bore. And the radius of curvature is quite independent of whether the bore is of the cylindrical or of the conical type.*

The Extrapolated Zero-head and its Connection with the Surface-Tension.

According to Professor Christiansen's view the length h_0, the extrapolated zero-head, which the extended $V^2 - h$ curve cuts off the axis of abscissæ is, as indicated above, determined by

$$\rho g h_0 = \frac{2C}{d'}$$

in which d', as will be remembered, denotes the diameter of the jet. The results of the experiments here described were, briefly, the following. With *cylindrical bores*, the $V^2 - h$ curve is rectilinear, Fig. 6. If extended

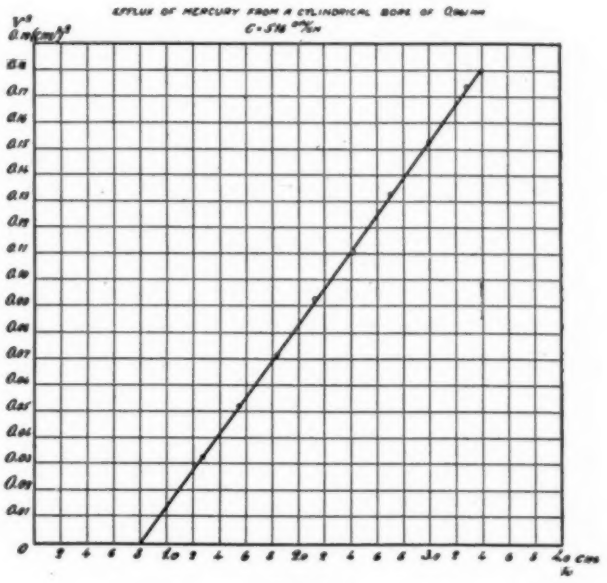


Fig. 6.

down to the axis of abscissæ it cuts off from the same length h_0, which, introduced in the formula above, always gives the same value for C, when d' is replaced by the diameter d of the jet-hole—in accordance with the fact of the actual contraction with cylindrical bores being nought. With *conical bores* the $V^2 - h$ curve is curvilinear, Fig. 7. If

extended to intersection with the axis of abscissæ by means of a flexible ruler and if the portion cut off is introduced in the formula for h_0 and if furthermore d', as in the case of the cylindrical bores, is replaced by the

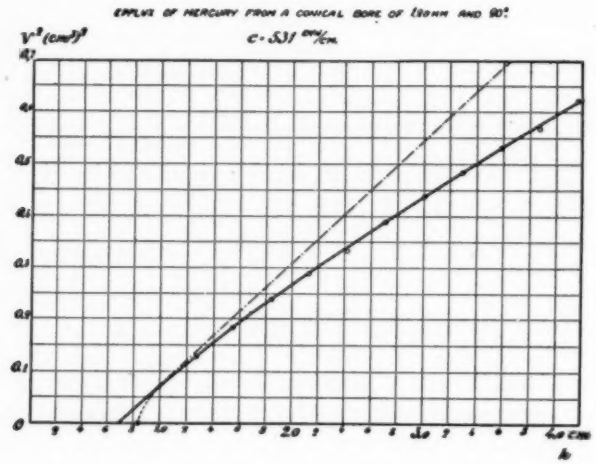


Fig. 7.

diameter d of the jet-hole,—*corresponding to the fact that the actual contraction with decreasing velocity tends to zero*[1]—one again obtains for C a constant value and mainly the same as with cylindrical bores. The common C-value very nearly coincides with those determinations of the surface-tension of mercury considered for the present time as the most reliable.

In order to illustrate how exactly the $V^2 - h$ curve, both at jets with and without contraction, passes through the point of the axis of abscissæ corresponding to the surface-tension C a series of values for this latter constant found in the course of the investigation is given in the following table.

TABLE I.

No.	Diameter of the Jet-hole.	Length of the Cylindrical Part of the Bore.	C.	Comment.
5.....	0.799 mm.	2.0 mm.	506 dyn./cm.	Cylindrical bores in steel. The C-values have been corrected for the drop of pressure in the cylindrical part of the bores. (See below.)
4.....	0.961	1.2	516	
6.....	1.218	3.0	527	
9 and 10.	1.507	2.5	507	

Mean, 514 dyn./cm. at about 15°.

[1] The statements concerning the contraction reproduce the results of a series of experiments carried out by the author.

TABLE II.

No.	Diameter of the Jet-hole.	Thickness of the Carton.	C.	Comment.
85.....	1.228 mm.	0.25 mm.	530 dyn./cm.	Holes pressed in carton, Fig. 8. The jet shows a variable contraction.
91 *A–B*..	1.923	0.13	547	
93.....	1.228	0.25	548	
94.....	0.965	0.13	532	
95.....	0.952	0.13	540	
96.....	1.380	0.13	522	

Mean, 536 dyn./cm. at about 16°.

As will be seen from the numbers of the experiments the figures in the first table represent results from some of the very first determinations, and these must be regarded exclusively as orientative. On the other hand the second table contains the latest and final determinations of the whole series of experiments. The true value of the surface-tension at 20° of a fresh mercury surface seems to be about 540 dyn./cm. In order to illustrate the accuracy which was reached in the later experiments No. 94 is reproduced in Fig. 9 diminished linearly in the ratio of about 3 to 1.

Fig. 8.

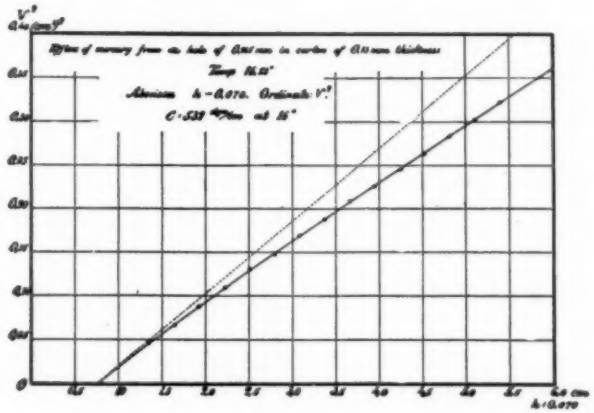


Fig. 9.

B. EXPERIMENTS WITH WATER.

Conditions of Experiments. Changes in the Aspect of the Jet During the Efflux. Cessation of the Efflux.

With a jet-hole in metal or glass it is impossible to carry out a unique experiment of efflux at low head with water or practically any other

liquid. This is due to the liquid wetting the surface of the hole-plate. A quantity of liquid accumulates around the jet-hole assuming the form indicated in Fig. 10. With heads of 3–4 cm. a jet is pressed through this mass and the jet stands with a sharp and smooth surface, but the liquid volume flowing out per sec. may vary several per cent. owing to the accidental variations in the form of the liquid mass. And it can be several per cent. larger than the volume which would flow out at the same head if the jet stood with a sharp edge against the hole plate. At a somewhat lower but still at a relatively high pressure the efflux in the form of a jet entirely ceases, the water draining down along the vertical surface of the hole plate. The adhesion of the water to the hole plate thus practically renders impossible the observation of the lower part of the normal $V^2 - h$ curve, and as a consequence hereof also the extrapolation to the zero-head h_0.

Fig. 10.

But it is possible to carry out practically just as reliable experiments with water as with mercury when, in the case of the first liquid, paraffin, or what is still better, paraffined paper, is used for the production of the hole plate. Water behaves in precisely the same manner towards paraffin as mercury towards iron. Thus a complete experiment of efflux is possible and during such an experiment quite the same variations are observed in the appearance of the jet as is described above for the mercury jet. Particularly distinct is the abrupt transition at low pressures from a long smooth jet to the pulsating form of efflux which again at a still smaller head alters to a smooth jet. Fig. 11, *a–c*, represents instantaneous photographs of the three consecutive phases of the efflux. Fairly characteristic is the abrupt manner in which the continuous part of the jet ends in the case of pulsating efflux. When the head sinks under a certain limit the efflux in form of a jet ceases and hereafter the water drains down along the wall of the hole plate. At a still smaller head h_0' the efflux suddenly stops and the water now stands with a convex

Fig. 11, *a–c*.

surface across the aperture of the jet hole, just as in the case of mercury. The certainty with which h_0' can be measured is, however, not so great with water as with mercury. Thus in one case the following repeated values of the last observed tapped-out portion were found

$$29.4 - 24.5 - 38.4 - 40.8 \text{ cm.}^3.$$

It seems that a systematic variation appears in this series. Four experiments gave for h_0' the values indicated in the following table:

Experiment.	Radius r of the Bore.	h_0'.	r'.	r'/r.
No. 61.....	0.735 mm.	1.318 cm.	1.137 mm.	1.55
74.....	0.885	1.051	1.427	1.61
63.....	0.901	0.945	1.590	1.76
73.....	1.091	0.713	2.064	1.89

In the table r' denotes the radius of the convex surface calculated from the expression

$$\frac{2C}{r'} = h_0'g,$$

in which for C—the surface-tension of the water—the value 73.6 dyn./cm. has been used.

The ratio of r' and r, the radius of the jet-hole, increases, as will be seen, with the radius of the jet-hole. The wider the hole is the more flat the curved surface seems to be. The experiments Nos. 61 and 63 were carried out with cylindrical bores in solid paraffin, Nos. 73 and 74 with holes pierced in paraffined paper.

The Zero-head and the Surface-tension.

The result of the test of Professor Christiansen's assumption was for water quite the same as for mercury. The extrapolated zero-head, h_0, determines the surface-tension of water when introduced into the expression $\rho g h_0 = 2C/d'$ given above when d' in this expression is put equal to the diameter d of the jet-hole. The certainty with which the surface-tension can be measured appears from the following summary of some of the determinations.

The experiments of Table I. must be regarded as to some degree orientative. In the experiments of Table II. the sources of error were examined with care and as to Table III. the numbers herein represent

TABLE I.

Experiment.	*d.*	C. Distilled Water.	C. Water from the Pipes.	Comment.
No. 32.....	1.019 mm.	74.8 dyn./cm.	—— dyn./cm.	Short cylindrical bores in paraffin with conical entrance.
30.....	1.220	74.4	——	
33(26)..	1.591	75.2	75.3	
34(25)..	1.996	70.0	70.0	
31.....	2.211	73.0	——	

Mean, 73.5 dyn./cm. at about 10°.

TABLE II.

Experiment.	Length of the Bores.	*d.*	*C* Uncorrected.	*C* Corrected.	Comment.
No. 57 ..	0.5 cm.	1.616 mm.	70.7 dyn./cm.	70.2 dyn./cm.	Cylindrical bores in paraffin. The inner edge rounded.
58 ..	0.2	1.567	77.1	71.1	
59 ..	0.1	1.698	80.3	72.3	
60 ..	0.4	1.442	88.5	72.9	
61 ..	0.8	1.470	101.3	72.6	
62 ..	0.8	2.490	96.0	73.9	
63	0.8	1.801	90.7	70.5	

Mean, 71.8 dyn./cm.

Corrected for different faults: 74.8 dyn./cm. at about 10°.

TABLE III.

Experiment.	Thickness of the Hole-plate	*d.*	*C.*	Comment.
No. 108....	0.17 mm.	1.628 mm.	72.8 dyn./cm.	Holes pierced in paraffined paper. Inner edge rounded.
118....	0.17	1.624	74.8	
111....	0.17	1.878	74.4	
109....	0.38	1.868	74.1	

Mean 74.0 dyn./cm. at about 10°.

the latest and presumably best of all the measurements. As will be seen, all *C*-values are situated very close to 74.0 dyn./cm., *i.e.*, the value which ordinarily is considered the true one for the surface-tension of water at 10°. Other series of experiments were carried out which mainly gave the same result. The series Nos. 49–55, carried out with cylindrical bores with conical entrance, gave for *C* the value 72.4 dyn./cm. at 10°. The series Nos. 71–74*b* (8 determinations at largely varying temperatures) gave $C = 73.4$ dyn./cm. at 10°. Finally from the isolated experi-

ment, No. 69, the value 75.2 dyn./cm. at 10° was found by means of curvilinear extrapolation.[1] In order to show with what degree of certainty the $V^2 - h$ curve could be determined in these experiments, and besides to illustrate the extrapolation carried out,—experiment No. 108 is reproduced in Fig. 12.

Thus water, as far as the question of the relation between h_0 and C is concerned, gave quite the same result as mercury. *The counter-pressure of the surface-tension is directly measured by* h_0.

The Friction-loss in a Longer Cylindrical Bore.

In Table II. above, heading the last column, a correction is indicated which will now be explained. In the preceding column the values of C which are directly evaluated from the $V^2 - h$ curves are reproduced. As will be seen, these values are as a whole too high and increasing with the length and narrowness of the cylindrical bore. In all probability the reason for this must be sought in the friction of the water in the bore and the author tried to calculate a correction for the error based on the

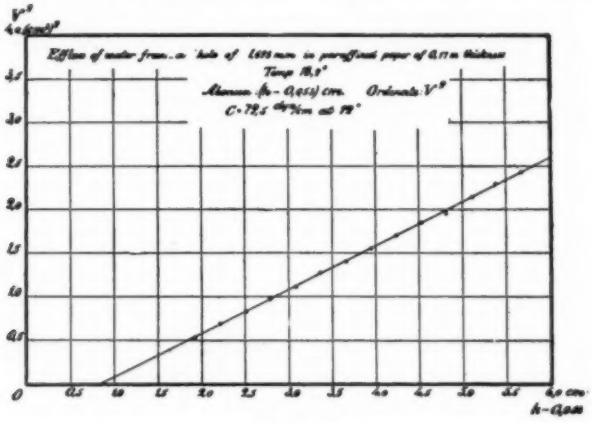


Fig. 12.

assumption that the friction in the bore is equivalent to a loss of pressure h_p which might be evaluated by means of Poiseuilles's expression, *i.e.*, by

$$h_p = \frac{128 \cdot \eta \cdot L}{\pi d^4 g} \cdot V,$$

where η is the coefficient of the viscosity of water at the temperature of the experiment, L the length of the bore and V the volume of liquid which flows out per sec.

[1] Holes pierced in paraffined carton ordinarily gave a rectilinear $V^2 - h$ curve. In the experiment No. 69 the carton was rather thin and the internal edge probably has been fairly sharp, so that an actual contraction has been present.

The volume V should accordingly be given by

$$V = \frac{\pi}{4} \kappa'^2 d^2 \cdot \sqrt{2g(h - h_0 - h_p)}$$

instead of by

$$V = \frac{\pi}{4} \kappa^2 d^2 \sqrt{2g(h - h_0)}$$

I now reduced the actual $V^2 - h$ curve to that which would have been observed if h_p had not existed. The reduction was carried out as indicated in Fig. 13. The values of h_p were calculated for two or three points and the abscissæ of these points were diminished by the h_p values. The original $V^2 - h$ curve which was in the main rectilinear or which perhaps had a hardly perceptible downward bend was thereby changed into a new, almost rectilinear but somewhat steeper $V^2 - h$ curve, the rectilinear extension of which cuts off an interval from the axis of abscissæ given, as will be seen from Table II., by

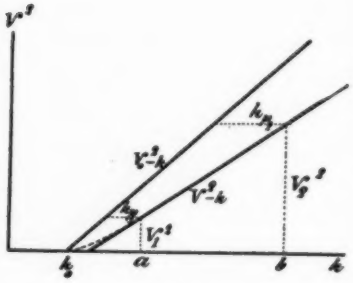


Fig. 13.

$$\frac{2C}{d} = h_0 g.$$

In the calculation of h_p the value of η corresponding to a parallel flow of the liquid is used. In order to give an idea of an experiment treated in the manner here described the experiment No. 60 is shown in Fig. 14.

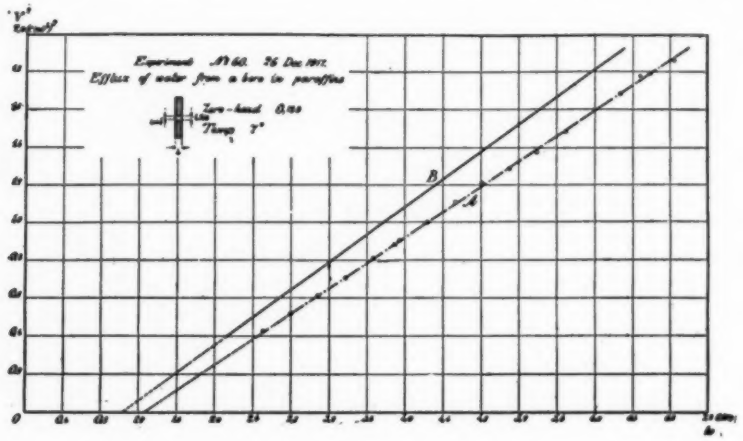


Fig. 14.

On the Influence of Ether vapor on the Surface-tension of Water.

The author found it worth while to repeat the old well-known experiment on the influence of ether vapor on the surface-tension of water. In the experiment a short cylindrical bore with a diameter of 1.278 mm. in solid paraffin was used. The experiment was carried on in such a way that the time of efflux for each of the normal portions of 50.2 mm.^{3} was observed on the jet being emitted into air, and also when a small piece of cotton saturated with ether was placed just above and close to the jet. In Fig. 15 the result of this double experiment is shown. It

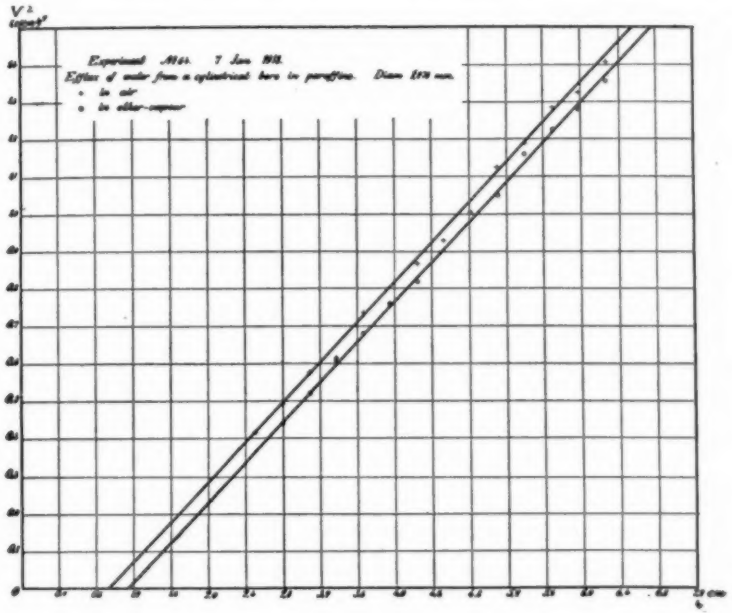


Fig. 15.

will be noticed that the $V^2 - h$ curve with ether vapor is exactly parallel to the curve with pure air. This suggests that the effect of the ether vapor is almost instantaneous, otherwise it would hardly be immaterial whether the jet has a velocity of 30 cm./sec. as is the case in the lower points of the curve—or 60 cm./sec. as is the case of the higher. Moreover, it will be observed that the uncertainty of the points is not greater with ether vapor than with pure air. This makes it probable that it is the maximum effect of the ether vapor which is dealt with, *i.e.*, the effect which in all probability should be observed at the efflux into an atmosphere of pure ether vapor. The change of the surface-tension amounts, as will be seen, to 18 per cent. It is of course most pronounced with the smallest velocities of the jet. Here the effect is extremely striking and

can easily be demonstrated in the following way. When the jet in air assumes the pulsating form described above it is observed on introducing the ether vapor that it straightens out and changes into a perfectly smooth and continuous jet, indicating that the counter-pressure of the surface-tension has partly been removed.

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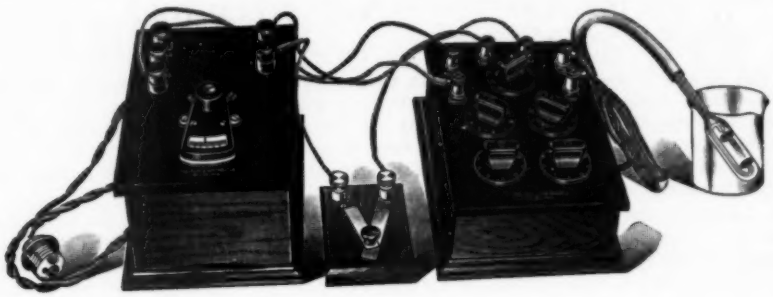

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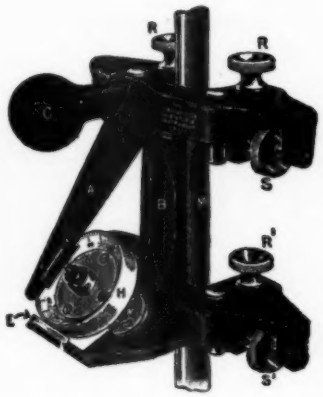

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The Synchronous motor may be shown by carefully increasing the frequency of the alternating current generated by increasing the speed of the central handle and at the same time have the armature connected to this alternating current and the field coils in the proper order connected to direct current.

The alternating current generator may be demonstrated by energizing the fields by direct current and using the armature that has the slip rings on it.

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In the preparation of synopses, authors should be guided by the following rules, which are illustrated by the synopses in the PHYSICAL REVIEW for January, February and March, 1920.* The new information contained in an article should first be determined by a careful analysis; then the subtitles should be formulated; and finally the text should be written and checked.

Rules

1. *Material not new* need not be analyzed or described; a valuable summary of previous work, however, should be noted.

2. *The subtitles should together include all the new information;* that is, every measurement, observation, method, improvement of apparatus, suggestion and theory which is presented by the author as new and of value in itself.

3. *Each subtitle should describe the corresponding information so precisely* that the chance of any investigator being misled into thinking the article contains the particular information he desires when it does not, or *vice-versa*, may be small. "X-ray patterns of metals" is too broad unless all metals have been studied, for an investigator may be interested, at the time, in only one metal; but "X-ray patterns of aluminum, effect of rolling" evidently satisfies this rule. It is particularly desirable that ranges of variation of temperature, wave-length, pressure, etc., be given in the subtitle.

General subtitles, such as "Object" or "Results," should not be employed, as they do not help to describe the specific information given in the article.

4. *The text should summarize the author's conclusions and should transcribe numerical results of general interest,* including those that might be looked for in a table of physical and chemical constants, with an indication of the accuracy of each. It should give all the information that anyone, not a specialist in the particular field involved, might care to have in his note book.

5. *The text should be divided into as many paragraphs* as there are distinct subjects concerning which information is given. Parts of subtitles may be scattered through the text but the subject of each paragraph, however short, must be indicated at the beginning.

6. *Complete sentences* should be used except in the case of subtitles. The synopsis should be made as readable as the necessary brevity will permit.

*The rules and illustrative synopses were prepared by G. S. Fulcher of the National Research Council.

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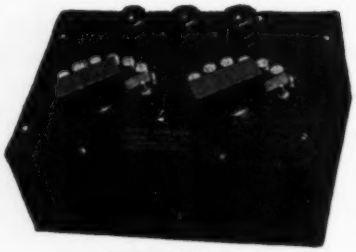

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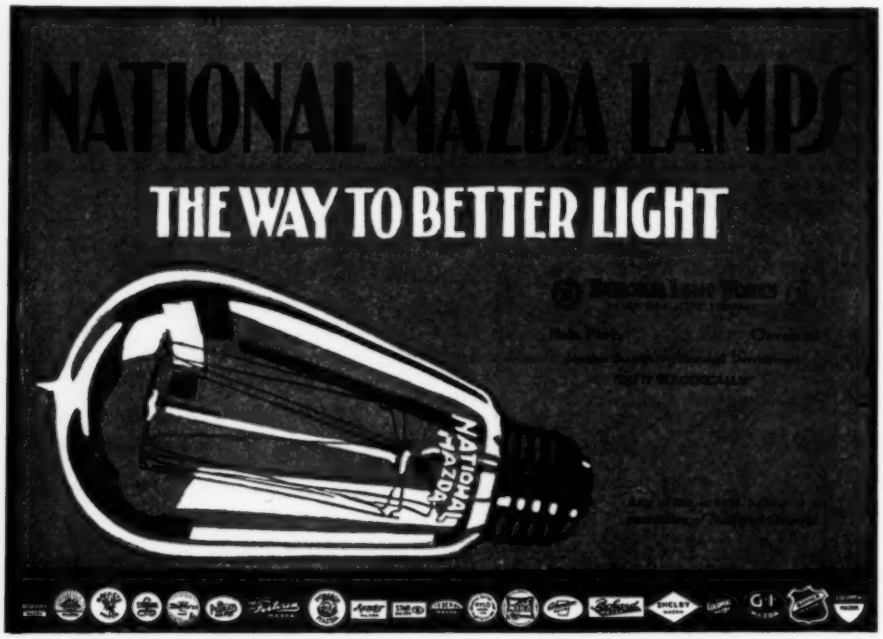

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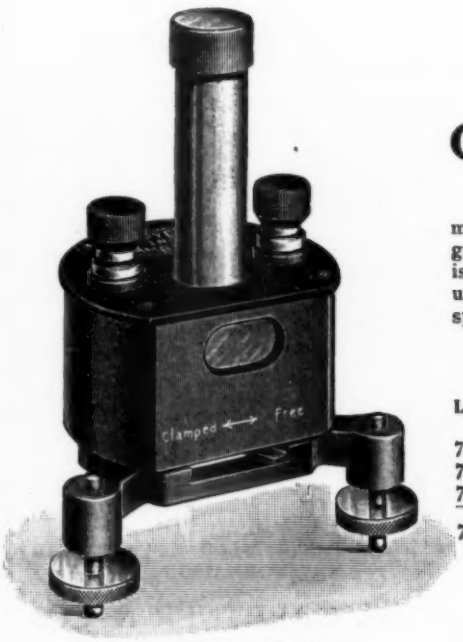

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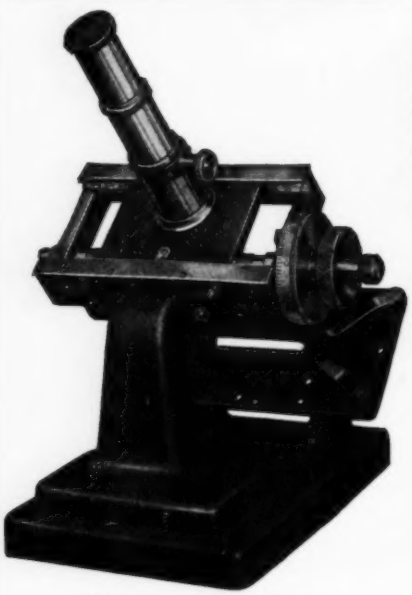

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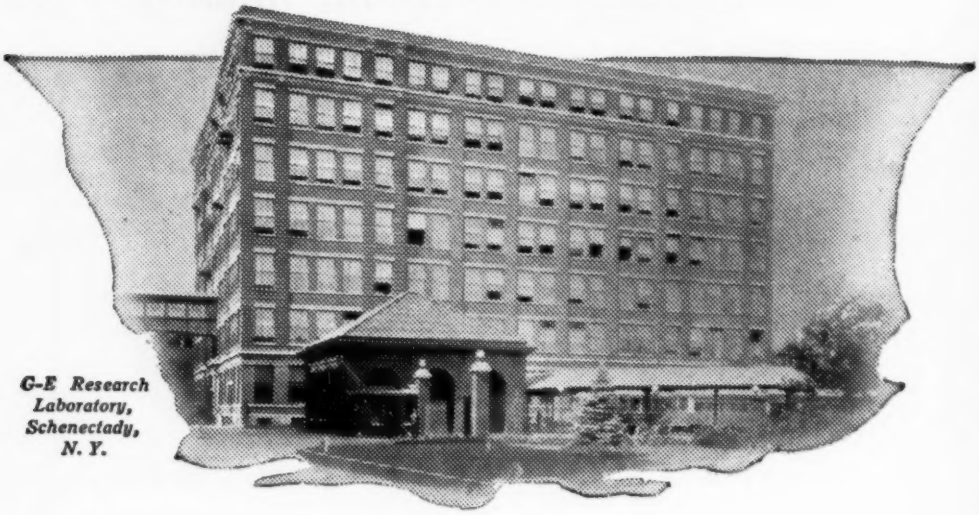

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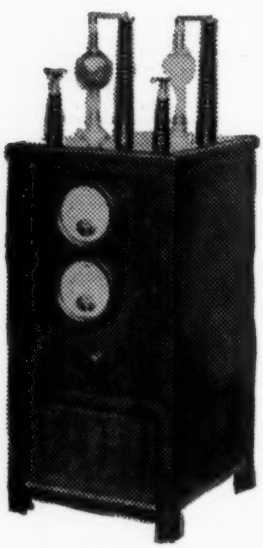

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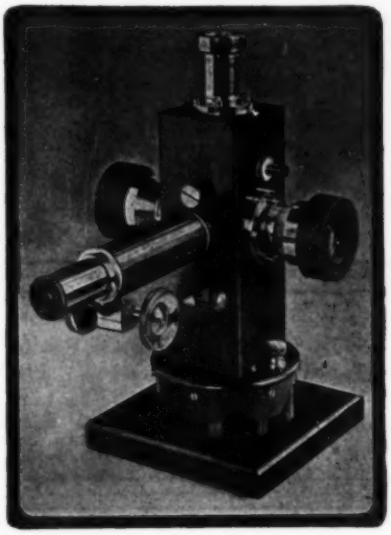

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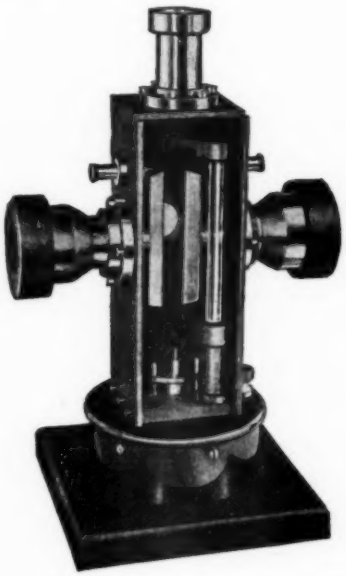

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